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Guidelines for the Use of Chemicals in Removing Hazardous Substance Discharges

Calspan Corp.
Buffalo, NY

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GUIDELINES FOR THE USE OF CHEMICALS IN REMOVING HAZARDOUS SUBSTANCE DISCHARGES

by

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16. ABSTRACT

This report was undertaken to develop guidelines on the use of various chemical and biological agents to mitigate discharge of hazardous substances. Eight categories of mitigative agents and their potential uses in removing hazardous substances discharged on land and in waterways are discussed.. The agents are classified as follows: (1) Mass Transfer Media; (2) Absorbents; (3) Thickening and Gelling Agents; (4) Biological Treatment Agents; (5) Dispersing Agents; (6) Precipitating Agents; (7) Neutralizing Agents; and (8) Oxidizing Agents.

The classification of each agent is developed in terms of: (a) Characteristic properties of the mitigative agent; (b) Potential spill situations on which the agent could be used; (c) The effects on the environment caused by use of the agent; (d) Possible toxic side effects caused by byproduct formation; and (e) Recommendations for use of the agent.

A countermeasure matrix that references various classes of mitigative agents recommended for treatment of hazardous substances involved in spills near or into a watercourse has been developed and includes a listing of hazardous chemicals, the corresponding EPA toxicity classification, and the physical properties of the chemical.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory (MERL) develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The detrimental impact on the environment due to discharges of chemical pollutants is often compounded by the potential toxic side effects caused by misuse of chemical and biological agents during mitigation of the spilled pollutant. The MERL Office of Research and Development recognized the importance of this potential hazard and directed this successful study to develop guidelines on the use of various agents to mitigate discharges of hazardous materials.

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Eight categories of mitigative agents and their potential uses in removing hazardous substances discharged on land and in waterways are discussed. The agents are classified as follows: (1) Mass Transfer Media, (2) Absorbents, (3) Thickening and Gelling Agents, (4) Biological Treatment Agents, (5) Dispersing Agents, (6) Precipitating Agents, (7) Neutralizing Agents, and (8) Oxidizing Agents.

The classification of each agent is developed in terms of:

(a) Characteristic properties of the mitigative agent

(b) Potential spill situations in which the agent could be used

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(e) Recommendations for use of the agent

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SECTION 1

INTRODUCTION

OBJECTIVE

The objective of this program, sponsored under EPA Contract 68-03-2093, Exhibit B, was to conduct a research and development project to determine guidelines for the use of chemicals to remove hazardous substance discharges from the environment. These guidelines are to be used by the EPA in the future to expand and revise Annex X of the National Oil and Hazardous Substance Pollution Contingency Plan CFR40, Chapter V, Part 1510, to include specific reference to chemical use for spills of hazardous substances. The guidelines develop the rationale to determine under what circumstances the use of chemicals or other additives is harmful to the environment.

SCOPE

Guidelines are established for the use of various chemicals and other additives to mitigate and remove spills of hazardous substances. These chemicals and other additives are currently addressed only in general terms by the statement of intent in Annex X, paragraph 2001,4: "no harmful quantities of any substances be applied to the waters to remove or mitigate the effect of oil and hazardous substances discharges."

Specific tasks were undertaken to address eight classes of mitigation agents. These are summarized below:

1. Mass Transfer Media: Determine under what circumstances it is permissible to add mass transfer media to a water column with no provision for removing the spent media and the ecological consequences of applying the media to a stream at the incorrect place such that the spill plume is missed completely.

2. Absorbents: Since absorbents are used routinely in oil spill mitigation, and may be chemically attacked by some hazardous substances, guidelines for their use shall be established.

3. Thickening and Gelling Agents: Determine under what circumstances these agents may be used in spill mitigation. The effects of unretrieved agents upon the environment shall be considered.

4. Biological Treatment Agents: Determine under what circumstances biological treatment agents may be appropriate for treating hazardous spilled materials.

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5. Dispersing Agents: Determine under what conditions dispersing agents may be used as a mitigating agent.

6. Precipitating Agents: Determine whether or not precipitate or precipitated ion, redissolved by chemical or microbiological means, are threats to the food chains.

7. Neutralizing Agents: Determine the circumstances that would dictate the use of neutralizing agents to decontaminate a spill of an acid or base and their effective use under the constraint of minimal environmental stress. The byproducts of neutralization and the potential biological damage that may be caused by overtreatment, undertreatment, or no treatment at all.

8. Oxidizing Agents: Determine under what circumstances oxidizing agents may be used for treating spills in a watercourse. Recognizing that these agents do not oxidize substances to CO_2 and H_2O, oxidizing agents that only result in innocuous byproducts should be considered.

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SECTION 2

SUMMARY AND CONCLUSIONS

The use of chemicals to mitigate hazardous substance spills can be justified only with proper controls and understanding of the secondary harmful effects they have on the environment. It is highly recommended that the hazardous spilled material be removed, if possible, from the environment by mechanical means. This mechanism of mitigation does not introduce any material to the environment that may have harmful effects. However, before any chemical is added to a watercourse as a mitigation procedure, the effects of the chemical on the environment, as well as the byproducts produced, must be understood.

Many of the chemicals that can be used in a mitigation procedure are harmful to the environment. Also, the byproducts of a mitigating chemical agent and the spilled hazardous material can present an undesirable long-term harmful effect on the environment. Generally, these byproducts are not removed from the ground or watercourse and data are not available to determine the environmental consequences of these byproducts. The environmental harm caused by the spill must be weighed against that of the mitigation agent and byproducts.

In order to minimize the harmful effects of a chemical mitigation agent, there must be adequate analytical monitoring during the entire mitigation procedure. Only with analytical monitoring can the on-scene coordinator (OSC) know where the hazardous material has spread with respect to the spill site and its concentration profile. This information is required in order that the OSC can determine which, if any, countermeasure should be used, where to counteract the spill, how much agent should be added to the watercourse, and when to cease mitigation procedures. Monitoring is an essential requirement in all mitigation procedures that must be accomplished with trained personnel using up-to-date equipment and analytical procedures at the spill scene.

Chemicals used in the mitigation of spills react differently with hazardous substances. Therefore, agents have been divided into eight categories (see Table 1). Chemicals and other additives were evaluated in each agent category. Emphasis was placed on the harmful effect that the mitigation agents would have if they were not retrieved and left in the environment.

Mass Transfer Media: Within this category, activated carbon and ion exchange resins were evaluated. The use of activated carbon for purification of potable water and food industries indicates that it is nontoxic to the human environment. The bioassay indicated that activated carbon is nontoxic unless it is used in massive quantities. In this situation, the activated carbon

TABLE 1. MITIGATION CATEGORIES

1. Mass transfer media
2. Absorbing agents
3. Gelling and thickening agents
4. Biological treatment agents
5. Dispersing agents
6. Precipitating agents
7. Neutralizing agents
8. Oxidizing agents

physically interferes with the respiratory function of the gills, causing a harmful effect. Inadequate data exist for evaluation of irretrievable activated carbon on benthic organisms.

The mechanism of the interaction between hazardous material and activated carbon is not clearly understood. The efficiency of activated carbon is increased with either high concentrations of pollutant or with compounds with low solubility. Organic material in general does not readily desorb. However, acid herbicides (i.e., 2,4-D and 2,4,5-T) and phenylurea herbicides (i.e., Diuros) readily desorb. The persistence of contaminated activated carbon left in the watercourse is not known even though the contaminated agent will act as a substrate for biodegradation. Data on the long-term toxicity of the hazardous-material-activated carbon are not available in the literature. The toxic material may be released at sub-toxic concentrations. Activated carbon is manufactured in many forms. The spill situation (hazardous chemical and watercourse parameters) will dictate which form of activated carbon is most efficient.

Ion exchange resins are used routinely in the food industry and in water purification. Some resins are ingested directly to reduce salt (Na+) intake. No evidence is available to indicate that exchange resins are toxic to the environment. The toxicity of exchange groups is generally low. All available evidence suggests that uncontaminated ion exchange resins would not produce toxicity problems if left in the environment. The mechanism of ion exchange resins is a one-to-one exchange of ionic species. The condition to regenerate the resin is by treating the resin with caustic or strong acid. These conditions will not readily occur in the environment. The desorption rate of hazardous material is not known. Therefore, the persistence of a toxic effect cannot be adequately addressed.

Because the desorption rates of many hazardous chemicals from mass transfer media in natural surface water is not known, it is not possible to evaluate the chronic toxicity problems that may be associated with the use of irretrievable agents. It may be safely recommended that irretrievable mass transfer agents be used to relieve the acute toxicity problems of spills of materials that degrade rapidly to nontoxic forms in natural surface water. It is also safe to recommend that such agents be used to mitigate acute effects of spills of other materials when it can be shown that the dispersed rate is such as to reduce total concentration (free + bound concentration) to nontoxic levels before desorption can occur. More research is required on desorption rates and dispersal rates to adequately define when the latter conditions exist.

Absorbing Agents: The available data on the use of absorbing agents pertain to oil and petroleum products. Natural absorbing products (i.e., straw, sawdust) are routinely used in oil mitigation. However, the spilled material readily desorbs and must be removed from the environment. There are several synthetic materials available for mitigating hydrophobic chemicals. These agents are nontoxic themselves and do not present a hazard to the environment in the uncontaminated state. However, desorption is significant since the agents can be regenerated by squeezing or wringing out the spent agent to be used again. There are some synthetic materials that can be used for mitigating hydrophillic chemicals. However, the desorption rate is again very high.

It may be concluded that absorbent materials are acceptable agents for spill treatment only under those circumstances in which the contaminated sorbent can be removed. Thus their use in water spills is limited to treatment of those materials that are insoluble and float. They are applicable in land spills of any materials that are effectively absorbed.

Thickening and Gelling Agents: Thickening and gelling agents are really special cases of absorbing agents. Their purpose in spill treatment is to immobilize the spilled material to prevent further spread into the environment and to condition the spill for mechanical removal. Like other absorbents, effective thickening and gelling agents are appropriate for use on all land spills and on water spills of organic liquids that float.

Manufacturers usually claim that these agents are nontoxic to the environment, but supporting data are not always presented.

Biological Treatment Agents: Biological treatment agents have previously been used in treating oil and oil-derived products. The method of mitigation is feasible on several other classes of organic materials. However, there are limitations to the technique as a general mitigation procedure. The time involved for biological degradation requires that the spilled hazardous material be contained and isolated from the environment for treatment. Otherwise, treatment is uncontrollable. The microbes that are added to the spilled material must be supplied with the essential nutrients to allow adequate growth. This implies that a culture maintenance program must be initiated. A third consideration is whether the ecological system will be maintained in balance. Microbes should not be introduced into the environment that will cause any significant change to the ecological balance. Data on the long-term effects of

biodegradation (i.e., the toxicity of byproducts and bioamplification) are not available in the literature.

The use of biological treatment agents for mitigation of hazardous spills is generally not appropriate except when the contaminated environment can be contained for sufficient time to permit detoxification. In general, it is recommended that other spill treatment agents be used whenever possible.

Dispersing Agents: Dispersing agents can be used to increase the rate of biodegradation of spilled material, to avoid damage to fowl by removal of oil and other organic materials from the water surface, to minimize fire hazard, and prevent contamination of beaches and solid objects.

Some dispersants are themselves toxic. Others are not. Some pollutants are more toxic after disposal than before disposal. It is necessary in each case to determine that the treatment does not increase toxicity of the spill before deciding upon its use.

Precipitating Agents: Precipitation is a valid mitigation technique for removing metal ions from solutions. Many metal ions can be precipitated with hydroxide ions at high pH. However, these salts will re-enter the water column when the pH returns to neutral, thereby causing a long-term hazard to the environment.

Sodium sulfide, when introduced as a solution into a spill, will precipitate heavy metal ions. At toxic concentration of heavy metal ions, an insoluble metal sulfide will form and reduce toxicity rapidly.

The sulfide ion and the hydrogen sulfide toxicity require that the sodium sulfide contain a strong base such as NaOH to raise the pH to inhibit H_2S formation. After treatment, the water column should be aerated if possible to remove residual hydrogen sulfide byproducts. The metal sulfide is sufficiently insoluble to reduce to a nontoxic level any reentry of metal ions into the environment.

Neutralizing Agents: Neutralization is an acceptable treatment for all spills of acids or bases provided some method for monitoring pH is available. Whenever possible, neutralization should be accomplished on land spills before the spilled material enters aquifers or surface water. After the spilled material has entered surface waters the toxicity associated with the change in pH from natural conditions is usually most critical. Neutralization of spills of large quantities of material is usually appropriate regardless of the neutralization agent available. However, when a choice of agents is available, it is extremely important to select the agent that produces the least toxic reaction products in returning the pH to normal. In some cases, post-treatment for toxic metallic ions may be necessary. All other considerations being equal, some advantage can be obtained by selecting weak agents as opposed to strong agents. Depending on the nature of the spilled material, some advantages can be obtained by selection of neutralization agents with optimum physical characteristics, but it is usually advisable to avoid use of solid agents when possible.

Temperature changes associated with exothermic neutralization reactions can produce secondary thermal pollution but this problem appears to be of secondary importance. Caution should be observed to avoid personnel injury due to sputtering or bubbling caused by exothermic reactions.

When the monitoring system is not sufficiently accurate to assure treatment to exactly the desired pH, it is usually better to undertreat than to risk overtreatment. pH values between 6 and 9 are acceptable.

Oxidizing Agents: Oxidizing agents are toxic to most organisms at low concentrations. Oxidation reactions are extremely difficult to control and seldom go to completion. Toxic intermediate reaction products are often left in the environment unless excess oxidizing agent is available. The agents are nonspecific and react with most organic materials.

The potential hazards in use of oxidizing agents for spill mitigation are so great that they are recommended only as a last resort and then only on land spills and water spills that are completely contained.

Mitigation Countermeasure Matrix: A mitigation countermeasure-hazardous substance matrix has been prepared to summarize the countermeasures that are effective on the EPA-proposed hazardous substances. This countermeasure matrix (see Section 5) is based on the chemical and biological literature. Where data are available, the secondary environmental effects were considered.

SECTION 3

RECOMMENDATIONS

The available literature contains little information on the effectiveness of mitigation agents in treating hazardous substance discharges. Many mitigating agents (i.e., oxidizers, neutralizers, precipitators) are themselves toxic if used in excess. Because of the variety of spill scenarios that exist, the potential toxic effect of excess agent cannot be properly addressed.

The effectiveness of a mitigating agent depends heavily on the specific spill situation. The amount of agent needed to counteract a hazardous substance discharge can be determined only for the academic situation of a laboratory evaluation. The spill conditions will vary in a real-life encounter. The size of the watercourse can range from a small pond to a large lake, such as the Great Lakes, to the ocean along the seacoast.

The conditions of flow can also vary from a slow-moving, low-flow creek during summer to a high-volume, turbulent river during spring.

The possible number of varied conditions of a watercourse dictate that a classification system must be formulated and agreed upon. A mitigation procedure that is applicable for one spill scenario could be totally inappropriate for another. For example, biological treatment agents may be effective for a spill in an isolated small pond, but would not be suitable in a turbulent river.

Only after this has been achieved can the effectiveness of a mitigation procedure and the long-term toxic effects of irretrievable contaminated agents and byproducts be adequately determined. It is recommended that a research program be initiated to formulate a classification system of spill scenarios. The persistence of toxic material in the environment, either treated or untreated, will be a factor in the selection of a countermeasure when the mitigating agent is not retrievable. The treatment will reduce the acute toxic effect of the hazardous substance discharge. The long-term toxic effect of the hazardous substance/mitigating agent complex may present an undesirable situation. The available literature indicates a lack of data to determine this potential hazard to the environment. It is recommended that a research program be initiated to determine the long-term toxic effect of irretrievable mitigating agents that have been contaminated with hazardous materials. This program should address itself to the reentry of the hazardous material into the ecosystem and the toxicity of the contaminated mitigation agent.

The rationale for the use of chemicals and other additives to counteract a discharge of a hazardous substance has been made based upon the available

chemical and biological literature. The literature contains information that can be applied to the mitigation process only in the ideal laboratory situations. There is little available information on the application of the mitigating agents to spills. It is recommended that a research program be initiated to determine the limitations of chemical mitigating agents under different field conditions.

Based on the available chemical and biological literature, recommendations for the use of chemicals and other additives are made. The following recommendations are made with respect to the classes of mitigating agents (mass transfer media, absorbing, thickening and gelling, biological treatment, dispersing, precipitating, oxidizing, and neutralizing).

Mass Transfer Media: Available evidence indicates that activated carbon or ion exchange resins introduced in moderate amounts to the aquatic environment will not in themselves be toxic. Confirmatory bioassay testing is recommended to more precisely determine concentrations which various fish and benthic organisms may tolerate.

Potential persistence of toxic organic compounds in the aquatic environment, both in solution and bound to mass transfer media, must be a factor in decisions relative to the use of irretrievable mass transfer agents for spill treatment. It may be safely assumed that:

1. Those toxic substances that are readily removed from the solution by biological processes in natural surface water are also readily removed by these processes when bound to mass transfer media.

2. The total toxic effect of those biodegradable materials can be reduced if acute toxicity is minimized by use of irretrievable mass transfer media,and natural biological processes are relied upon to prevent chronic toxicity that would otherwise occur as a result of desorption processes that are expected in natural surface waters.

Therefore, it is recommended that the use of irretrievable mass transfer media be considered acceptable for treatment of that class of materials that are biodegradable under all conditions.

Those materials that are not quickly degraded to nontoxic products in the natural environment cannot be expected to degrade more rapidly in the bound condition. Even though acute toxicity of a spill of such materials can be reduced by use of irretrievable mass transfer media, a serious chronic problem could result with desorption. Under special circumstances in which it can be shown that dispersion would reduce total contaminant concentration (i.e., in solution and bound to mass transfer media) to nontoxic levels before desorption could occur, the use of mass transfer media to alleviate the acute toxicity problem would still be appropriate. Additional research on dispersion rates, toxicity levels, and desorption rates would be required to permit the on-scene coordinator to establish when those circumstances exist. We recommend that such research be performed. Until the results of that research are available, we recommend that irretrievable mass transfer media be considered appropriate for treatment of spills of such materials only as a last resort.

Absorbing Agents: It is recommended that the use of absorbents, both natural and synthetic, be authorized for treatment of spills only in those situations in which the sorbent can be removed from the environment. For water spills, utility is therefore limited to organic liquids that are insoluble and float. For land spills, natural sorbents are useful for all liquids, and synthetics for all organics that are absorbed.

Thickening and Gelling Agents: It is recommended that thickening and gelling agents, either as specific compounds or as blended agents, be considered appropriate for use in treatment of land spills of all liquid materials on which they are effective. Individual agents should be considered appropriate for treatment of water spills of insoluble organics that float.

Thickening and gelling agents should not be used on water spills of materials that sink or mix into the water column.

More research is required to determine the effectiveness and behavior of blended gelling agents in water before general recommendations can be made relative to application to water spills.

Biological Treatment Agents: It is recommended that biological agents be considered appropriate for mitigating spills of those materials that are biodegradable, but only for those cases in which the contaminated medium can be contained. Because of the difficulty in controlling biological processes and variables that affect them, it is recommended that other mitigation agents be used for spill treatment whenever possible.

Dispersing Agents: The advantages of using dispersants to treat spills are: (1) the rate of biodegradation is increased, (2) damage to marine fowl is avoided since oil or other hazardous material is removed from the water surface, (3) the fire hazard from the spill is reduced by dispersion of the hazardous material several feet into the water column, (4) the spill is prevented from wetting solid surfaces such as beach sand and shore property, and (5) natural dilution is enhanced.

Dispersants are recommended as desirable additions to enhance the biological degradation of spilled material. However, they must be chosen with care and the quantity used carefully controlled to avoid unnecessary harm to aquatic life. Prior to the use of dispersants on a specific spilled substance, it should be established through research that no increase in toxicity will result from the dispersed substance or the degradation product of the added dispersant.

Precipitating Agents: It is recommended that a solution of sodium sulfide stabilized with sodium hydroxide be used as a precipitating agent for heavy metal ions. The reentry of heavy metal sulfide precipitate into the watercourse will be sufficiently small to minimize any secondary toxic effects unless the heavy metal sulfide is converted to an organo metallic salt (e.g., mercury salts). Further study is required to determine the chronic effect of metal salts in the water system.

Neutralizing Agents: It is recommended that neutralization be used as

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the primary treatment for all spills of acids and bases that are sufficiently large as to create an environmental problem. Adequate monitoring is necessary for all spill treatment. Treatment should be accomplished on land whenever possible (i.e., before the spilled material flows into surface water).

In most spills of acids or bases, the principal toxic problem is caused by the change in pH. In general, the return of pH to normal values reduces toxicity regardless of neutralization agent used. It is recommended, however, that care be taken when possible to select a neutralization agent that produces the least toxic byproducts in the neutralization reaction. It is further recommended that other considerations being equal, weak acids and weak bases be selected in preference to strong acids and bases as treatment agents. By so doing, potential for overtreatment can be minimized.

Oxidizing Agents: Because of a variety of potential problems with the use of oxidizing agents in spill control, it is recommended that their use be limited to land spills and water spills that are completely contained. Oxidants should be used on land and in surface waters only when no other spill mitigation measure is available and only when the spilled material can be contained for sufficient time to permit accurate control and monitoring of the treatment.

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SECTION 4

SPILL MITIGATION MEASURES

This section discusses some of the parameters that enter into the decision-making process used by the on-scene coordinator and what specific countermeasures are effective for particular hazardous substance discharges. The mitigation process has been divided into classes. The biological and chemical literature was reviewed to evaluate various countermeasures. The possible toxic effect of countermeasure agents was evaluated to determine the acute toxicity of the agent and the long-term toxicity and persistence of the nonretrieved agent contaminated with hazardous substances.

MASS TRANSFER MEDIA

This category of countermeasures involves use of those agents that will remove the hazardous substance from the watercourse either by adsorption (e.g., activated carbon) or by mass transfer (e.g., ion exchange resins).

There is no doubt that the acute toxicity of many spills can be substantially reduced by treatment with mass transfer media. When irretrievable mass transfer media are used, a potential exists for desorption of the spilled materials to proceed at such a rate as to create a chronic toxicity problem. Some of these materials have been identified, but others probably exist. Current literature is inadequate. Therefore, it is recommended that the general use of mass transfer media for spill treatment be limited to those spill materials that degrade naturally to nontoxic products in uncontaminated surface water. The effectiveness of treatment therefore is limited to the mitigation of the acute toxicity problem.

In special cases, such as in large, fast-flowing streams where it can be accurately determined that dispersion produces total contaminant concentration (i.e., free + bound) to nontoxic levels before desorption can occur, the use of mass transfer media would also be applicable. Additional research on desorption rates, toxicity levels, and dispersion rates would be required to establish those conditions that constitute special cases.

Activated carbon is produced from organic materials by heating in the absence of air to drive off volatiles followed by steam or sometimes chemical treatment to increase porosity. The most common raw materials used for activated carbon production are coal and lignin.

There is much evidence indicating the relative nontoxicity of activated carbon to man. Carbon for water purification has been used over the ages. In 1817, Thomas Thompson (1) stated, "when putrid water at sea is mixed with about

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1/9th its weight with charcoal powder, it is rendered quite fresh." Activated carbon is still routinely used to remove tastes and odors from potable water supplied either by filtration through carbon beds or direct introduction of carbon slurries to water supply reservoirs.

The direct introduction of powdered carbon into water supply reservoirs has been used for algae control as well as taste and odor control. Dosages for algae purposes are small, in the order of one to a few parts per million. However, dosages are repeated, sometimes on a daily basis, until the algae problem is eliminated. Activated carbon is not considered toxic per se to algae; rather, it reduces the penetration of light, thus reducing algal growth. The literature does not contain references related to effects on fish or benthic organisms when activated carbon is used for reservoir treatment. If significant fish kills occurred, one would expect documentation in the literature.

In a bioassay study on the toxicity of powdered activated carbon on fish (2) it was found that fathead minnows could survive short contact times in a 10% carbon slurry. The 24-hour LD_{50} (i.e., that water concentration at which half the test organisms survived over a 24-hour period) for fathead minnows in carbon-treated water was 30,000 ppm.

In water bodies, carbon will either settle to the bottom (with the exception of special floatable carbon such as AQUA NUCHAR C-190) in the immediate vicinity of the spill treatment, or be carried near or far downstream before settling.

In either case, the concentration of activated carbon should decrease rapidly after a single application since it behaves physically like silt in the water column.

Based on available evidence, the application of activated carbon alone to water bodies will not constitute a threat to human or aquatic life unless applied in massive quantities. Further bioassay testing, especially on the effects of activated carbon on benthic organisms, is recommended to confirm the concentration of carbon which the aquatic environment is able to assimilate without significant stress. Thus, with reservations pending results of those tests on benthic organisms, it is concluded that a single application of irretrievable activated carbon at the incorrect location (i.e., missing the spill plume) is not expected to present a serious ecological effect other than the temporary aesthetic problem.

Ion exchange resins consist of insoluble high-molecular-weight organic polymers containing charged functional groups that are able to exchange with either positive or negative ions in aqueous solution. Resins that exchange cations from functional groups for cations in solution are cation exchange resins. Resins that exchange anions from functional groups for anions in solution are anion exchange resins. In strong acid ion exchange resins, the functional group is normally a sulfonic group and weak acid ion exchange resins usually contain a carboxylic or phenolic group. The functional groups in strong base anion exchange resins are generally quarternary ammonium compounds and weak base anion exchangers employ an amino or imino functional group.

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Commercially available ion exchange resins employ H^+ and Na^+ as the predominant exchangeable cations while Cl^- and OH^- appear as the predominant exchangeable anions. The toxicity of the above ions is relatively low.

In a spill situation, depending on what material is spilled and what type of resin is used, there will be exchange of the spilled substance for one of the above. As an example, for a spill of a heavy metal salt of mercury using a strong acid ion exchange resin, the following occurs:

$$2RSO_3H + Hg^{+2} \rightarrow (RSO_3)_2Hg + 2H^+$$

where

R = Resin matrix

SO_3H = Functional group

It is of importance to note that exchange is stoichiometric, resulting in weight equivalent exchange.

The question arises as to whether or not the organic matrix or the functional groups of exchange resins are toxic to humans, fish or other aquatic organisms.

The relative human nontoxicity of ion exchange resins prepared according to specifications is supported by their use in the food and pharmaceutical industries. Ion exchange resins are used to purify water used in food preparation, purify water for use in manufacture of distilled alcoholic beverages, purification of pharmaceuticals, and color and other impurity removal from sugars. Resins are also ingested directly to reduce salt (Na^+) intake.

Ion exchange resins used in food and pharmaceutical preparation are subject to Food and Drug Administration (FDA) regulations. The regulations list the types of resins that can be used in the preparation of food based on composition of the resin matrix. There are 16 listed types of resin matrices including the more common ones identified in the regulations. The exchangeable cations or anions normally employed in exchange resins (i.e., H^+, Na^+, Cl^-, OH^-) are approved for use under proper conditions.

The regulations stipulate the procedures for use of ion exchange resins in food preparation, and testing and labeling requirements for ion exchange resins to be used in the treatment of food. It is of importance to note the very low solubility requirements in various solvents (no more than 1 ppm organic extractives in distilled water, alcohol, and acetic acid).

The differences between food and pharmaceutical and normal ion exchange production is the high degree of quality control and purification for the former. The use of approved food or pharmaceutical-grade ion exchange resins for spill treatment is not expected to pose any hazard to water for human consumption. These resins would also not be expected to be toxic to fish or aquatic organisms. However, direct evidence of nontoxicity to fish or aquatic life is not available. Confirmatory bioassay tests are recommended.

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It is also quite probable that ion exchange resins not having food or pharmaceutical approval would still not pose a threat to aquatic life or drinking water when used to treat spills. Recall that the differences in manufacture are mainly differences in quality control. If irretrievable ion exchange resins are introduced at the incorrect location, there will be some exchange with natural ionic material that occur in trace amounts in surface water. This may cause a temporary depletion of desirable ionic species but it is not expected to produce any significant problems.

Hazardous Pollutant Removal by Mass Transfer Media

In addition to selecting a nontoxic agent for hazardous spill treatment, it is highly desirable to select a treatment agent that gives the highest probability of effective spill treatment. The agent selected for treatment should be that which most effectively adsorbs or exchanges the spilled hazardous pollutant from solution, thereby rendering it less hazardous to the aquatic environment. The effectiveness of activated carbon and ion exchange resins for removal of specific organic and inorganic compounds from water (under ideal conditions of contact) were investigated.

The mechanisms of carbon adsorption and ion exchange have been examined with respect to prediction of the degree to which these media will remove organic and inorganic compounds from solution.

The mechanisms of carbon adsorption are not well understood, but empirical observation of adsorption phenomena have resulted in a number of generalizations that are of value in predicting adsorbability. It has been well demonstrated that both the rate and degree of carbon adsorption increase with the concentration of pollutant in water. The strategy of fast response to spills before extensive dilution is extremely important.

In general, it is found that carbon adsorption is more effective for compounds of low solubility (Lundelius' rule). Since solubility of organic compounds generally decreases with increasing chain length, it has been observed that adsorption from aqueous solution increases as a homologous series is ascended (Traube's rule). However, the rate of adsorption generally decreases with increasing molecular weight.

For organic compounds that are structurally simple, carbon adsorption is at a minimum for the charged species in water and at a maximum for neutral species. As compounds become more complex, effects of ionization become of decreasing importance.

The amenability of organic compounds to activated carbon was studied by Guisti et al. (3) with activated carbon dosages that were five times the pollutant concentration. Table 2 provides their data on the percent reduction of pollutant. This information can provide valuable assistance relative to the applicability of mass transfer agents for spills of specific substances, but cannot predict the degree of success for specific spill scenarios. The time to respond, water current, turbulence, and volume of water affected are other determinants of spill treatment effectiveness, as well as choice of treatment agent.

TABLE 2. AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION

Compound	Molecular Weight	Aqueous Solubility (%)	Concentration (mg/l) Initial (C_o)	Concentration (mg/l) Final (C_f)	Adsorbability* g Compound/ g Carbon	Adsorbability* Percent Reduction
Alcohols						
Methanol	32.0	∞	1000	964	0.007	3.6
Ethanol	46.1	∞	1000	901	0.020	10.0
Propanol	60.1	∞	1000	811	0.038	18.9
Butanol	74.1	7.7	1000	466	0.107	53.4
n-Amyl alcohol	88.2	1.7	1000	282	0.155	71.8
n-Hexanol	102.2	0.58	1000	45	0.191	95.5
Isopropanol	60.1	∞	1000	874	0.025	12.6
Allyl alcohol	58.1	∞	1010	789	0.024	21.9
Isobutanol	74.1	8.5	1000	581	0.084	41.9
t-Butanol	74.1	∞	1000	705	0.059	29.5
2-Ethyl butanol	102.2	0.43	1000	145	0.170	85.5
2-Ethyl hexanol	130.2	0.07	700	10	0.138	98.5
Aldehydes						
Formaldehyde	30.0	∞	1000	908	0.018	9.2
Acetaldehyde	44.1	∞	1000	881	0.022	11.9
Propionaldehyde	58.1	22.0	1000	723	0.057	27.7
Butyaldehyde	72.1	7.1	1000	472	0.106	52.8
Acrolein	56.1	20.6	1000	694	0.061	30.6
Crotonaldehyde	70.1	15.5	1000	544	0.092	45.6
Benzaldehyde	106.1	0.33	1000	60	0.188	94.0
Paraldehyde	132.2	10.5	1000	261	0.148	73.9
Amines						
Di-N-Propylamine	101.2	∞	1000	198	0.174	80.2
Butylamine	73.1	∞	1000	480	0.103	52.0
Di-N-Butylamine	129.3	∞	1000	130	0.174	87.0
Allylamine	57.1	∞	1000	686	0.063	31.4
Ethylenediamine	60.1	∞	1000	893	0.021	10.7
Diethylenetriamine	103.2	∞	1000	706	0.062	29.4
Monethanolamine	61.1	∞	1012	939	0.015	7.2
Diethanolamine	105.1	95.4	996	722	0.057	27.5
Triethanolamine	149.1	∞	1000	670	0.067	33.0
Monoisopropanolamine	75.1	∞	1000	800	0.040	20.0
Diisopropanolamine	133.2	87.0	1000	543	0.091	45.7
Pyridines & Morpholines						
Pyridine	79.1	∞	1000	527	0.095	47.3
2-Methyl 5-Ethyl pyridine	121.2	sl.sol.	1000	107	0.179	89.3
N-Methyl morpholine	101.2	∞	1000	575	0.085	42.5
N-Ethyl morpholine	115.2	∞	1000	467	0.107	53.3
Aromatics						
Benzene	78.1	0.07	416	21	0.080	95.0
Toluene	92.1	0.047	317	66	0.050	79.2
Ethylbenzene	106.2	0.02	115	18	0.019	84.3
Phenol	94.0	6.7	1000	194	0.161	80.6
Hydroquinone	110.1	6.0	1000	167	0.167	83.3
Aniline	93.1	3.4	1000	251	0.150	74.9
Styrene	104.2	0.03	180	18	0.028	88.8
Nitrobenzene	123.1	0.19	1023	44	0.196	95.6
Esters						
Methyl acetate	74.1	31.9	1030	760	0.054	26.2
Ethyl acetate	88.1	8.7	1000	495	0.100	50.5

* Dosage: 5 g Carbon C/l of solution.

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TABLE 2 (CONTINUED)

Compound	Molecular Weight	Aqueous Solubility (%)	Concentration (mg/l) Initial (C_o)	Concentration (mg/l) Final (C_f)	Adsorbability* g Compound/g Carbon	Adsorbability* Percent Reduction
Esters						
Propyl acetate	102.1	2.0	1000	248	0.149	75.2
Butyl acetate	116.2	0.68	1000	154	0.169	84.6
Primary amyl acetate	130.2	0.2	985	119	0.175	88.0
Isopropyl acetate	102.1	2.9	1000	319	0.137	68.1
Isobutyl acetate	116.2	0.63	1000	180	0.164	82.0
Vinyl acetate	86.1	2.8	1000	357	0.129	64.3
Ethylene glycol monoethyl ether acetate	132.2	22.9	1000	342	0.132	65.8
Ethyl acrylate	100.1	2.0	1015	226	0.157	77.7
Butyl acrylate	128.2	0.2	1000	43	0.193	95.9
Ethers						
Isopropyl ether	102.2	1.2	1023	203	0.162	80.0
Butyl ether	130.2	0.03	197	nil	0.039	100.0
Dichloroisopropyl ether	171.1	0.17	1008	nil	0.200	100.0
Clycols & Glycol Ethers						
Ethylene glycol	62.1	∞	1000	932	0.0136	6.8
Diethylene glycol	106.1	∞	1000	738	0.053	26.2
Triethylene glycol	150.2	∞	1000	477	0.105	52.3
Tetraethylene glycol	194.2	∞	1000	419	0.116	58.1
Propylene glycol	76.1	∞	1000	884	0.024	11.6
Dipropylene glycol	134.2	∞	1000	835	0.033	16.5
Hexylene glycol	118.2	∞	1000	386	0.122	61.4
Glycols & Glycol Ethers						
Ethylene glycol monomethyl ether	76.1	∞	1024	886	0.028	13.5
Ethylene glycol monoethyl ether	90.1	∞	1022	705	0.063	31.0
Ethylene glycol monobutyl ether	118.2	∞	1000	441	0.112	55.9
Ethylene glycol monohexyl ether	146.2	0.99	975	126	0.170	87.1
Diethylene glycol monoethyl ether	134.2	∞	1010	570	0.087	43.6
Diethylene glycol monobutyl ether	162.2	∞	1000	173	0.166	82.7
Ethoxytriglycol	178.2	∞	1000	303	0.139	69.7
Halogenated						
Ethylene dichloride	99.0	0.81	1000	189	0.163	81.1
Propylene dichloride	113.0	0.30	1000	71	0.183	92.9
Ketones						
Acetone	58.1	∞	1000	782	0.043	21.8
Methyl ethyl ketone	72.1	26.8	1000	532	0.094	46.8
Methyl propyl ketone	86.1	4.3	1000	305	0.139	69.5
Methyl butyl ketone	100.2	v.sl.sol.	983	191	0.159	80.7
Methyl isobutyl ketone	100.2	1.9	1000	152	0.169	84.8
Methyl isoamyl ketone	114.2	0.54	986	146	0.169	85.2
Diisobutyl ketone	142.2	0.05	300	nil	0.060	100.0
Cyclohexanone	98.2	2.5	1000	332	0.134	66.8
Acetophenone	120.1	0.55	1000	28	0.194	97.2
Isophorone	138.2	1.2	1000	34	0.193	96.6

* Dosage: 5 g Carbon C/l of solution.

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TABLE 2 (CONTINUED)

Compound	Molecular Weight	Aqueous Solubility (%)	Concentration (mg/l) Initial (C_o)	Concentration (mg/l) Final (C_f)	Adsorbability* g Compound/ g/Carbon	Adsorbability* Percent Reduction
Organic Acids						
Formic acid	46.0	∞	1000	765	0.047	23.5
Acetic acid	60.1	∞	1000	760	0.048	24.0
Propionic acid	74.1	∞	1000	674	0.065	32.6
Butyric acid	88.1	∞	1000	405	0.119	59.5
Valeric acid	102.1	2.4	1000	203	0.159	79.7
Caproic acid	116.2	1.1	1000	30	0.194	97.0
Acrylic acid	72.1	∞	1000	355	0.129	64.5
Benzoic acid	122.1	0.29	1000	89	0.183	91.1
Oxides						
Propylene oxide	58.1	40.5	1000	739	0.052	26.1
Styrene oxide	120.2	0.3	1000	47	0.190	95.3

* Dosage: 5 g Carbon C/l of solution.

The adsorption and desorption from ion exchange resins depend upon the exchange resin matrix and the chemical pollutant. The primary consideration is whether or not "strong" versus "weak" ion exchange resins are to be recommended for spill treatment. In strong acid ion exchange resins, the functional group is normally a sulfonic group such as $-SO_3H$ or $-SO_3Na$. A weak acid ion exchange resin usually contains a carboxylic (-COOH) or phenolic group (-OH). Weak acid cation exchangers normally exchange only the cations associated with weak acid salts such as bicarbonate, carbonates, and acetates. They generally do not react with cations of strong acid salts such as chlorides, sulfates, and nitrates. Therefore, strong acid cation exchange resins are preferable for general use for spilled substances amenable to cation exchange treatment.

The functional groups in strong-base anion exchange resins are generally quarternary ammonium compounds, while weak-base anion exchangers employ an amino or imino functional group. Weak-base anion exchangers usually do not exchange the anions associated with the salts of weak acids, whereas strong-base anion exchange resins exchange anions of both weak and strong acids and their salts. It is also pointed out in manufacturers' specifications for anion resins that weak-base anion exchange resins are effective only in the pH range 0 to 7, whereas strong-base anion exchange resins are effective in the entire pH range of 0 to 14. Thus, strong-base anion exchange resins have greater utility in spill treatment.

Desorption and Persistence of Hazardous Pollutants From Mass Transfer Media

Given that a hazardous substance is removed from surface water by activated carbon or an ion exchange resin, it is of importance to ascertain the extent to which desorption may occur and the biological consequences of this desorption. In addition, it is of importance to ascertain if toxic substances (captured) on carbon or ion exchange resins persist, or are chemically or biologically degraded to a less, or possibly more, toxic product.

Information from manufacturers and the literature indicates that desorption from activated carbon or ion exchange resins should not easily occur in natural waters. Normally, to strip carbon of the adsorbed organics or to remove exchanged ions from exchange resins, drastic changes of ambient conditions such as pH adjustment, solvent extraction, or heating at 1600°F to 1800°F and ion exchange resins are often regenerated by treatment with caustic or acid. Such extreme changes in ambient conditions would not be expected in natural water bodies.

Desorption from activated carbon by water alone has, however, been observed for some pesticides (4). Moderate amounts of acidic herbicides (2,4-D or 2,4,5-T) have been found to be readily desorbed from activated carbon by water. The phenylurea herbicides (Diuron and Monuron) have been found to be adsorbed on activated carbon in large amounts only to be readily desorbed in uncontaminated water.

The question posed with regard to the use of carbon or ion exchange resins on substances that may later exhibit desorption is whether desorption produces a greater toxicologic problem than if the agent were not used. The question of persistence in adsorbed or nonadsorbed states must be considered in overall evaluations.

There are no studies in the literature on the release of hazardous substances from ion exchange resins and resultant influence on fish or other aquatic organisms. It is apparent that further study is needed to more clearly establish the desorptive behavior of hazardous pollutants from activated carbon and ion exchange resins in the aquatic environment and subsequent influence on fish and benthic organisms.

As discussed previously, the degree to which organic pollutants persist in the aquatic environment in either adsorbed or unadsorbed states enters into decisions to treat hazardous substances with irretrievable mass transfer media. Ideally, treatment of a spilled hazardous organic substance with carbon or ion exchange resin will substantially reduce acute toxicity, followed by chemical and/or biological decomposition of the adsorbed organic to a nonhazardous substance. Persistence in the adsorbed state accompanied by chronic poisoning of the aquatic habitat is undesirable.

Washington University researchers compiled, organized, and interpreted a mass of data on the persistence of organic chemicals in dilute aquatic systems such as might be present in a quiescent lake (5). They reported degradation of organic compounds as a percent of the theoretical oxidation under various conditions including "as-is" river water, sewage seed, and acclimated activated sludge seed. The Washington State researchers then categorized the various organics into one of three groups:

1. Organic compounds readily removed from aquatic environment (Table 3),
2. Organic compounds removed from aquatic environment with acclimated microorganisms (Table 4), and
3. Organic compounds resistant to removal from aquatic environment.

TABLE 3. REPORTED ORGANIC COMPOUNDS READILY REMOVED FROM AQUATIC ENVIRONMENT

Compound	Technique	Ref.
Alcohols		
Allyl alcohol	BOD AS	375
Ethanol	Resp. AS	366
Glycerol	Resp. AS	429
Glycol	Resp. AS	429
n-Hexadecanol	RW CA-CO_2	319
p-Hydroxy benzoic acid	Resp. B	507
Methanol	Resp. AS	366
1,5-Pentanediol	BOD AS	375
Phenols		
o-Cresol	RW CA	159
m-Cresol	RW CA	159
p-Cresol	RW CA	159
1-Naphthol	RW CA	159
Phenol	RW CA	159
Aldehydes, Acids and Salts		
Furfural	RW CA	157
Acetic acid	Resp. AS	429
Citric acid	Resp. AS	429
Formic acid	Resp. AS	429
Lactic acid	Resp. AS	429
Mandolic acid	Resp. B	507
Oxalic acid	Resp. AS	429
Quinic acid	Resp. B	507
Tartaric acid	Resp. AS	429
Ammonium acetate	Resp. AS	429
Calcium formate	BOD AS	375
Calcium gluconate	Resp. AS	429
Ethyl formate	BOD AS	375
Phenyl acetate	Resp. B	507
Nitrogen Compounds		
Alanine	Resp. AS	429
Glutamic acid	Resp. AS	429
Glycine	Resp. AS	429
Miscellaneous		
2-Ethyl 3-propyl acrolein	BOD RW	499
Dextrin	Resp. AS	429
Glucose	Resp. AS	429
Starch	Resp. AS	429
Styrene	CA-CO_2	411
Xylose	Resp. AS	429

AS - Activated sludge seed
Resp. - Respirometer
RW - River water
CA - Chemical analysis
B - Bacterial culture

TABLE 4. REPORTED ORGANIC COMPOUNDS REMOVED FROM AQUATIC ENVIRONMENT WITH ACCLIMATED MICROORGANISMS

Compound	Technique	Ref.
Hydrocarbons		
n-Butyl benzene	Resp. AS	59
Ethyl benzene	Resp. AS	59
n-Propyl benzene	Resp. AS	59
Alcohols		
n-Amyl alcohol	BOD AS	219
sec-Amyl alcohol	BOD AS	219
Benzyl alcohol	Resp. AS	366
n-Butanol	Resp. AS	366
sec-Butanol	Resp. AS	366
tert-Butanol	Resp. AS	366
n-Dodecanol	Resp. AS	59
n-Hexanol	BOD AS	375
Isoamyl alcohol	BOD AS	219
Isobutanol	Resp. AS	366
Isopropanol	Resp. AS	366
Methanol	Resp. AS	137
4-Pentanol	BOD RW	499
n-Propanol	Resp. AS	366
Phenols		
o-Chlorophenol	CA RW	158
p-Chlorophenol	CA RW	158
Aldehydes, Ketones, Acids, Salts, and Ethers		
Acetaldehyde	Resp. AS	429
Benzaldehyde	BOD AS	375
Cinnamaldehyde	BOD RW	499
Crotonoldehyde	BOD RW	499
Formaldehyde	Resp. AS	429
2,4-Hexadienal	BOD RW	499
Methacrolein	BOD RW	499

Resp. - Respirometer
AS - Activated sludge seed
RW - River water
CA - Chemical analysis
BOD - Biological oxygen demand

(continued)

TABLE 4 (CONTINUED)

Compound	Technique	Ref.
Aldehydes, Ketones, Acids, Salts, and Ethers (continued)		
Propionaldehyde	BOD AS	219
Acetone	COD AS	219
Diethylketone	BOD AS	375
Methyl n-amyl ketone	BOD AS	375
Methyl isobutyl ketone	BOD AS	375
Methyl phenyl ketone	BOD AS	375
Methyl isopropyl ketone	BOD RW	499
Acrylic acid	CA-CO_2	411
Benzoic acid	BOD AS	153
Caproic acid	BOD AS	153
Formic acid	BOD AS	153
Heptanoic acid	BOD AS	153
Methacrylic acid	CA-CO_2	411
Valeric acid	BOD AS	153
Diethylene glycol monoethyl ether acetate	BOD AS	375
Diglycol diacetate	BOD AS	375
Ethylene dichloride	BOD AS	375
Propene oxide	COD AS	219
Methylmethacrylate	CA-CO_2	411
2 Methoxy ethylacetate	BOD AS	375
Sodium formate	Resp. AS	137
Sodium oleate	BOD AS	59
Sodium stearate	BOD AS	59
Vinyl acetate	CA-CO_2	411
Dimethoxy methane	COD AS	219
2-Ethoxy ethanol	BOD AS	59
2-Methoxy ethanol	BOD AS	375
Methyl phenyl ether	BOD AS	375
Triethylene glycol	BOD AS	375
Nitrogen Compounds		
Acetanilide	BOD RW	374
Acetonitrile	CA-N_2	331
Acetylethanolamine	BOD AS	375

Resp. - Respirometer
AS - Activated sludge seed
RW - River water
CA - Chemical analysis
BOD - Biological oxygen demand

(continued)

TABLE 4 (CONTINUED)

Compound	Technique	Ref.
Nitrogen Compounds (continued)		
Acrolein	BOD RW	499
Acrylamide	COD RW	104
Acrylonitrile	CA-N_2	331
Adiponitrile	CA-N_2	331
Anthranallic acid	Resp. AS	369
Arginine	BOD AS	153
Benzonitrile	CA-N_2	331
Diaminoethane	BOD RW	374
Diethanolamine	BOD AS	375
Lactonitrile	CA-RW-N_2	331
Leucine	BOD AS	153
Methionine	BOD AS	153
Monoethanolamine	BOD AS	375
Morpholine	BOD AS	375
Oxydipropionitrile	CA RW-N_2	331
Phenylalanine	BOD AS	153
3-Picoline	CA RW	156
Pyridine	CA RW	156
Threonine	BOD AS	153
Tryptophane	BOD AS	153
Tyrosine	BOD AS	153
Valine	BOD AS	153
Sulfur Compounds		
n-Butyl benzene sulfonate	BOD AS	457
sec-Butyl benzene solfonate	BOD AS	457
n-Dodecyl sodium sulfonate	BOD AS	464
Ethyl benzene sulfonate	BOD AS	457
Lauryl sulfate	BOD AS	464
Methyl benzene sulfonate	BOD AS	457
n-Octyl benzene sulfonate	BOD AS	457
sec-Octyl sulfonate	BOD AS	457
n-Propyl benzene sulfonate	BOD AS	457
sec-Propyl benzene sulfonate	BOD AS	457
Sodium benzene sulfonate	BOD AS	59

Resp. - Respirometer
AS - Activated sludge seed
RW - River water
CA - Chemical analysis
BOD - Biological oxygen demand

It appears reasonable to believe that organic compounds that readily degrade in water will also degrade in an aqueous system when adsorbed on carbon or are attached to ion exchange resins.

The mass transfer media should provide a good substrate for bacteria and other organisms to consume the adsorbed pollutant. Adsorption to reduce acute toxicity, followed by microbial degradation, appear to be a reasonable treatment sequence if degradation is reasonably fast and degradation products are not themselves significantly toxic. Bioassay tests to ascertain the degree to which adsorbed or ion exchanged hazardous substances degrade, and attendant toxicity phenomenon accompanying this degradation, are recommended.

It has been found in soil studies that, generally, adsorption of pesticides on soil and organic matter reduces toxicity. Concurrently, however, a number of pesticides, especially chlorinated hydrocarbons, have been found to persist for longer periods of time when adsorbed on soil or organic matter. Similar behavior appears reasonable when adsorption is on carbon or ion exchange resins. Studies of the persistence and toxicity of pesticides (and other hazardous pollutants) when adsorbed on activated carbon or ion exchange resins are recommended.

Conclusions and Recommendations

Available evidence indicated that activated carbon or ion exchange resins introduced in moderate amounts to the aquatic environment will not in themselves be toxic. Confirmatory bioassay testing is recommended to more precisely determine concentrations which various fish and benthic organisms may tolerate.

Potential persistence of toxic organic compounds in the aquatic environment, both in solution and bound to mass transfer media, must be a factor in decisions relative to the use of irretrievable mass transfer agents for spill treatment. It may be safely assumed that

1. Those toxic substances that are readily removed from the solution by biological processes in natural surface water are also readily removed by these processes when bound to mass transfer media, and

2. The total toxic effect of those biodegradable materials can be reduced if acute toxicity is minimized by use of irretrievable mass transfer media and natural biological processes are relied upon to prevent chronic toxicity that would otherwise occur as a result of desorption processes that are expected in natural surface waters.

Therefore, it is recommended that the use of irretrievable mass transfer media be considered acceptable under all conditions for treatment of that class of materials which are biodegradable. Specific materials that are known to be in this class are indicated in the countermeasure matrix presented in Section 5.

Those materials that are not quickly degraded to nontoxic products in the natural environment cannot be expected to degrade more rapidly in the bound condition. Even though acute toxicity of a spill of such materials can be

reduced by use of irretrievable mass transfer media, a serious chronic problem could result with desorption. Under special circumstances in which it can be shown that dispersion would reduce total contaminant concentration (i.e., in solution and bound to mass transfer media) to nontoxic levels before desorption could occur, the use of mass transfer media to alleviate the acute toxicity problem would still be appropriate. Additional research on dispersion rates, toxicity levels and desorption rates would be required to permit the on-scene coordinator to establish when those circumstances exist. We recommend that such research be performed. Until the results of that research are available, we recommend that irretrievable mass transfer media be considered appropriate for treatment of spills of such materials only as a last resort.

Activated carbon is sold in many forms from a fine powder to large granules. Multipurpose activated carbon that may be used in spill mitigation may be obtained from these companies:

American Novit Company
Calgon Corporation
ICI America, Ltd.
Westvaco Chemical Division
Union Carbide Corporation
Barneby-Cheney Company

Ion exchange resins are also sold in many forms by several manufacturers. Dow Chemical Company and Rohm and Haas Company manufacture and market a large variety of ion exchange resins that are appropriate for spill mitigation. We recommend that company representatives be contacted at the time of a spill to determine which available ion exchange resin is most appropriate for use on the specific material involved in the spill.

ABSORBENTS

The use of absorbents for treatment of spills of hazardous substances other than oil has not been practiced or even studied to a great extent. Available information indicates that absorbents would be of value for treatment of all land spills and of water spills of some organic materials. Use of absorbents for treatment of water spills will probably be limited to those substances that are insoluble and float on the water surface (i.e., that behave much like oil).

Absorbents can be divided into two general types: natural and synthetic. Natural absorbents include natural products such as vegetation residues including corn plant stalks and straw, and wood residues including sawdust and lignin. These natural materials have been used for years in mitigating oil spills. However, specific data are not available on their effectiveness for absorbing other organic liquids.

Absorbent materials derived from natural materials including straw, corn-based absorbents, and wood-based and others are presumed to be nontoxic though confirmatory data are not available. A large amount of these materials introduced into a water body could produce a high biological oxygen demand (BOD) upon degradation by microorganisms. Slowly degradable substances such as

lignin-based materials, or sawdust, would not be expected to impose as rapid biological oxygen demands as straw or other highly biodegradable organics.

Synthetic products have been made from various organic polymers including polypropylene, alklystyrene and polyurethane. They are specifically manufactured to absorb hydrophobic organic liquids while repelling hydrophillic liquid such as water. A review of commercial synthetic products shows that a variety of different polymers are used. Three commercial products that represent different types of organic polymers will be discussed:

1. 3M "Oil Absorbent" - polypropylene

2. Dow "Imbiber Beads" - cross-linked co-polymer

3. SSC "Absorbents" - polyurethane

3M Company "Oil Absorbent" is a white, fibrous polymer made from polypropylene, has a density of 0.91 and remains buoyant after saturation with oil and most other organic liquids. It is insoluble in water and resistant to all common solvents.

Dow imbiber beads are made from a number of lightly cross-linked polymers including alkylstyrene polymers or tertiary butyl polymers. The exact composition is unknown. The density of the imbiber heads varies from 0.95 to slightly over 1.0. A special property of Dow imbiber beads is their tendency to swell up to three diameter sizes upon imbibition of organics, including aromatic hydrocarbons, benzene, toluene, styrene and chlorohydrocarbons without dissolution of the polymer matrix. Imbiber beads are insoluble in water, methanol, or acetone.

SSC absorbents are prepared from specially treated polyurethanes. The nature of the "special" treatment is not given in product literature. SSC absorbents are also buoyant before and after oil adsorption.

Some information on toxicological properties of these commercial absorbents mentioned previously have been provided by the manufacturers. The "oil absorbent" which is 100% polypropylene is claimed as nonirritating to the skin and the eyes according to information provided to the U.S. Department of Labor by the 3M Company (6). However, protective gloves are advised for continuous handling. Communication with 3M Company (7) reveals that this material has FDA approval for use in removing oils from household foodstuffs such as gravy. It can be considered, therefore, as nontoxic to humans. Bioassay test data with fish and other aquatic organisms is not available, although it may be reasonably assumed that polypropylene is nontoxic to fish.

Communications with Dow Chemical (8) reveal that some of the imbiber bead products have undergone bioassay tests and have been approved for use as absorbents by the State of California, State Water Resources Control Board. As such, they have been ascertained to be nontoxic to fish.

The Sorbent Sciences Corporation (SSC) has shown that their polyurethane absorbent material is nontoxic to brine shrimp and California killfish in

concentrations ranging from 0.5 gm/l to 10.0 gm/l. Bioassay tests were conducted over 72-hour periods according to Standard Methods for the Examination of Water and Wastewater. The SSC absorbent material has also been approved for use as a collecting agent by the State of California, State Water Resources Control Board, based on results of bioassay testing.

In addition to bioassay tests, SSC tested degradation of polyurethane absorbents in sea water. There was no weight loss over a 20-day period, indicating that biodegradation or chemical degradation of the product does not occur in sea water.

Treatment Effectiveness

There are no data indicating the extent to which natural materials such as straw, ground corn cobs, sawdust, etc. will absorb organic liquids other than oil. Various companies have provided some data on synthetic product absorption of specific organic liquids or classes of organic liquids. Most data that have been provided concerns absorption of pure organic liquids. This information can be reasonably extrapolated to ascertain the effectiveness of the agents for land spills. In cases where spills occur in water, estimates of removal effectiveness cannot be directly inferred from the data on absorption of pure liquids. Extrapolation is reasonable for highly insoluble organic liquids that float on the water surface.

The 3M Company provided data on the absorption capacity of its polypropylene absorbent for a number of pure organic liquids, as given below:

Chemical	Absorption Capacity, g Chemical/g Sorbent
Hexane	7.4
Benzene	10.0
Naphtha	8.5
Kerosene	8.2
Freon 133	15.8
Chloroform	17.8
Ethyl ether	8.1
Ethyl acetate	10.7
Butyraldehyde	8.8
Methyl ethyl ketone	11.9
n-Amyl alcohol	10.9
Polyethylene glycol 400 MW	4.2
Methanol	12.1
Dimethyl formamide	15.4

These data pertain to pure organic liquids and are therefore applicable for land spills. Beginning with ethyl ether and proceeding downward, the named substances are highly soluble or miscible with water. Absorption of these substances from water is therefore expected to be poor according to 3M (9).

Dow imbiber beads can be custom-made to absorb specific substances. They are generally made of alkylstyrene tertiary butyl copolymers. The copolymers are claimed to be capable of absorbing a number of organic liquids including the following (10):

Linear aliphatics such as hexane and gasoline

No. 1, 2 and 3 fuel oils

Chlorinated solvents such as methylchloroform and trichlorobenzene

Aromatic solvents such as benzene, styrene, and methylnaphthalene

Some polar materials including methylisobutylketone, ether, and tetrahydrofuron

A partial listing of specific substances that are said to be imbibed by one type of Dow cross-linked swellable polymer (Imbiber Bead "S") includes the following:

cumene
divinyl benzene
ethyl benzene
benzene
pyridine

toluene
Chlorobenzene
dichlorobenzene
benzyl chloride
methyl bromide

xylenes
epichlorohydrin
dibromochloropropane
styrene
trichlorofluoromethane

chloroform
chloromethane
dichlorodifluoromethane
perchloroethylene

trichloroethylene
halogenated hydrocarbons
ethylene dichloride
trichlorobenzene/PCB mixtures

In addition to imbibition of hydrocarbons floating on the surface of the water, imbiber beads have been shown to remove kerosene, toluene, and benzene that were dissolved in water up to saturation. Removal by agitated contact with cross-linked alkylstyrene polymers was 74% for dissolved kerosene, 95.9%

for dissolved toluene, and 96.5% for dissolved benzene (11).

The SSC specially treated polyurethane foam is claimed to pick up low- and high-viscosity oil, paint, petrochemicals, tar, vegetable oils, and many other organic materials from water surfaces. Storage capacity of 40 to 60 times the weight of the absorbent is claimed.

Of the two categories of absorbents (natural and synthetic), there are little data available to estimate the absorption of organic liquids other than oil by natural absorbents. The limited data given in previous sections of this report give some guidance, but perhaps not all that is needed for complete tabulation of organic liquid treatment using synthetic absorbents. As a general rule, it appears that polar substances with appreciable solubility or miscibility with water must be rated as poorly removed by synthetic absorbents. In addition, dense organic liquids that sink in the water column cannot be effectively removed by absorbents. The problem is relating the degree of organic liquid solubility to a treatment rating for synthetic absorbents in terms of "good," "fair," and "poor" removability from water. There is little data to provide guidance in rating the many substances under consideration on the proposed "hazardous substance list."

The synthetic absorbent material has been designed for organic material based on chemical theory. Therefore, they are not expected to be efficient in the absorption of inorganic liquids.

Desorption and Persistence of Hazardous Pollutants from Absorbents

Natural absorbents such as straw and corn will absorb oil and perhaps similar organics only from surfaces having thick floating deposits. Desorption from these materials is known to be significant. Removal of oil-soaked or other organic-soaked straw and other natural absorbents is imperative for effective spill treatment. In a similar manner, most synthetic absorbents only loosely absorb oil and other organic liquids. Wringing or squeezing the absorbed organics from the synthetic absorbents for reuse is claimed to be logistically advantageous as well as cost effective.

A notable exception to the above types of absorbents are the swellable imbiber beads as represented by the Dow Chemical alkylstyrene tertiary butyl-copolymers. It is claimed to be impossible to squeeze imbibed organic liquids from the Dow imbiber bead products (12). In this case, the pollutant would either not be released back to the aquatic environment, or be released at only a slow rate. Retrieval of the pollutant-saturated imbiber beads from the spill environment does not appear to be as critical for this type of absorbent. Biodegradation of absorbed pollutants and residual toxicity of pollutant-laden imbiber beads must be ascertained through bioassay testing, however, before a recommendation can be made for their use as irretrievable agents.

Recommendations

It is recommended that the use of absorbents, both natural and synthetic, be authorized for treatment of spills only in those situations in which the absorbent can be removed from the environment. For water spills, utility is

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therefore limited to organic liquids that are insoluble and float. For land spills, natural absorbents are useful for all liquids, and synthetics for all organics that are absorbed.

Absorbents that are applicable for organic liquids may be obtained from several manufacturers:

BASF Wyandotte Corporation
B.F. Goodrich Company
Mine Safety Appliances
Dow Chemical Company
Rohm and Haas
Phillips Petroleum Company
Union Carbide
Sorbent Sciences Corporation
3M Company

THICKENING AND GELLING AGENTS

Thickening and gelling agents are really a subclass of absorbent. Their purpose in spill treatment is to immobilize the spilled material to prevent further spread into the environment and to condition the spill for mechanical removal. Like other absorbents, effective thickening and gelling agents are appropriate for use on all land spills and in some cases they may be appropriate for water spills of organic liquids that float.

Under previous contracts (EPA 68-01-0110 and 68-03-2093) Calspan evaluated a wide variety of thickeners and gelling agents for spill treatment. Most commercially available materials were found to require vigorous mixing of the agents with the spilled material and/or temperature control of the mixture to promote thickening. None was effective on all classes of liquid chemicals. However, materials were found to be specifically effective for thickening four general classes of potential spill materials.

Natural proteinaceous compounds (i.e., gelatine) can be used for gelling hazardous aqueous solutions, but water-soluble polyelectrolyte polymers such as Gelgard M (Dow Chemical) and Kelzan (Kelco) were found to be most effective for thickening most water-soluble liquids.

Imbiber beads (the Dow Chemical product discussed previously) were found to be most effective for gelling nonpolar organic liquids.

Three polymers, Hycar 1422 (a polyacrylonitrile-butadine copolymer produced by B.F. Goodrich), Soloid (a Kelco, Inc. derivative of xanthan gum), and Klucel (a hydroxypropyl cellulose polymer by Hercules Corp.) were shown effective on polar and chlorinated organic liquids.

Alcohols were effectively gelled by Carbopol 934 (B.F. Goodrich), a polyacrylate polymer, and Klucel (mentioned above for polar organics).

The agents described above can be used independently to congeal ground spills of the materials of the chemical classes with which they are associated

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above. As indicated earlier, imbiber beads can also be used on water spills of insoluble materials that float on water. In an effort to produce a single agent that would be effective for congealing all liquid spills, Calspan (under EPA sponsorship) blended four of the agents described above to produce a multipurpose gelling agent according to the following recipe:

Gelgard M	5%
Imbiber beads	30%
Carbopol 934	25%
Hycar 1422	30%
Cabosil	10%

Cabosil is a fluidizing agent produced by Cabot Corporation, and was incorporated to promote ease of application. With this recipe the multipurpose gelling agent was found to be effective for congealing all liquids tested with a dosage of approximately 1 pound of agent to 1 gallon of spilled liquid. Table 5 lists the test liquids used in evaluating the multipurpose gelling agent.

Toxicity of Gelling Agents

There is very little toxicity data available on synthetic polymers used as thickeners or gelling agents. The manufacturers state without presenting supporting data that their products are nontoxic. The toxicity of irretrievable agents that have gelled hazardous substance is not known. There is also no data on the rate of desorption from the gelled mass.

TABLE 5. LIQUIDS TESTED WITH MULTIPURPOSE GELLING AGENT

Acetone	Formaldehyde
Acetone cyanohydrin	Gasoline
Acrylonitrile	Isoprene
Ammonium hydroxide	Isopropanol
Analine	Kerosene
Benzaldehyde	Methanol
Benzene	Methyl ethyl ketone
Butanol	Octane
Carbon disulfide	O-dichlorobenzene
Carbon tetrachloride	Petroleum ether
Chlorine water (saturated)	Phenol (89%)
Chloroform	Pyridine
Cyclohexane	Sulfuric acid
Ethanol	Trichloroethylene
Ethylacetate	Water
Ethylene Dichloride	Zylene
Ethylene Glycol	

Further research must be performed to determine the secondary toxic effects of irretrievable gelling agents with and without the absorbed hazardous material.

Recommendations

It is recommended that thickening and gelling agents, either as specific compounds or as blended agents, be considered appropriate for use in treatment of land spills of all liquid materials on which they are effective. Individual agents should be considered appropriate for treatment of water spills of insoluble organics that float. Thickening and gelling agents should not be used on water spills of materials that sink or mix into the water column.

More research is required to determine the effectiveness and behavior of blended gelling agents in water before recommendations can be made relative to application to water spills.

BIOLOGICAL TREATMENT AGENTS

The use of biological agents has been restricted, for the most part, to treatment of oil and oil derivatives or components, and is still not a common practice in emergency spill treatment. In principle, microbial degradation may be effective for a variety of hydrocarbons. Although there are many limitations on the use of biological degradation, the advantage of this method of dealing with spills is that it is a natural means of removal through biochemical breakdown. The spill may be attacked in situ, in areas inaccessible to other methods of treatment, at a minimum of cost and effort if conditions are appropriate. In addition, biological treatment may be utilized as a supplemental tool to other methods of spill treatment.

Biological agents for the mitigation of organic liquids is recommended only if (1) the spill is contained (i.e., as in a pond or stream that may be dammed), (2) sufficient time is available for biodegradation, and (3) the introduction of the microbes will not be detrimental to the existing environment. The spilled material must be contained to allow sufficient time for bacterial population growth.

The actual growth of bacteria applied to a spilled material will be influenced by many factors: the culture viability, length of lag phase, acclimation, growth requirements, temperature, oxygen availability, type of substrate, surface availability, and contact time.

As a general rule, the life cycle of a bacteria population includes four reasonably distinct phases. Upon innoculation into a new medium, the cycle begins with a lag phase, which is not a quiescent stage, but one of synthesis of new kinds of enzymes and adjustment to the chemical and physical environment (Figure 1). The length of the lag phase is dependent upon the physiological condition of the bacteria, the innoculum dosage, acclimation and other effects. Addition of essential nutrients, such as nitrogen and phosphorus, to the spilled material may speed or enhance growth and shorten the length of the lag period. These nutrients may be added in the form of ammonium chloride (NH_4Cl), phosphoric acid (H_3PO_4), or sodium hexametaphosphate $(NaPO_3)_6$.

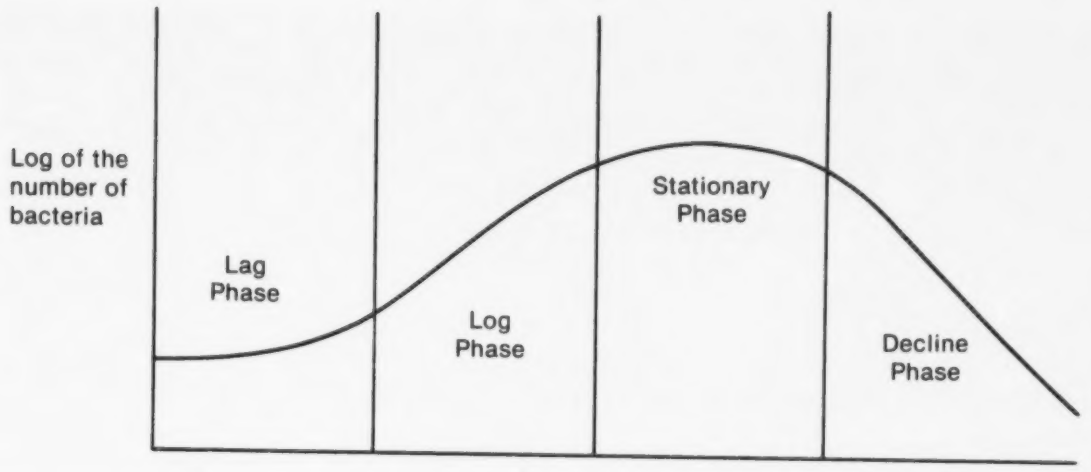

Figure 1. Bacterial growth phases.

A period of rapid growth, known as the log or experimental phase, characteristically follows the lag phase when conditions are satisfactory for growth. The third phase, termed stationary, is characterized by a constancy due to either complete cessation of cell division or to the balancing of reproduction rate by the death rate. Finally, a death phase ensues in which the death rate exceeds the reproduction rate. It is often possible to prolong the log and stationary phases by the re-addition of nutrients essential to growth, unless a buildup of inhibitory products of degradation prevents new growth.

The length of the lag time is critical to the effectiveness of using microbial degradation to combat spills. In some spill situations, the rapid dispersion of spilled material may make such a countermeasure completely impractical. The most practical step that might be taken to minimize this problem is containment of the spill. Use of cultures that are acclimated to the chemicals being treated can be of significant advantage, but would not necessarily solve the problem. For example, in one experiment bacteria in activated sludge acclimated to aniline required 192 hours to oxidize 34% of the phenol added. Bacteria acclimated to phenol required only 12 hours to oxidize 39% of the same material (13). In another case, acclimated bacteria removed 95% of phenol in 24 hours while unacclimated bacteria of the same culture removed only 24% in 23 hours (14). There are significant reductions in lag time, but it would not be sufficient under many spill conditions unless the spilled material is contained.

The effectiveness of biological treatment of toxic materials is dependent upon several variables that cannot be fully controlled in spill situations.

Oxygen is essential for aerobic degradation. In most situations where the spill is contained, natural aeration is probably inadequate for rapid detoxification, and some method for forced aeration will be required. Agitators, compressed air-bubble systems, or spray systems could be used where equipment is available.

Temperature affects the acclimation of bacteria, rate of bacteria growth, and overall effectiveness of treatment. In most cases temperature cannot be controlled. Where it could be controlled, elevated temperatures would usually increase the rate of bacterial growth and thus treatment rates, but may result in increased toxicity of spilled material, degradation products or additives used as part of the treatment.

The nature of the spilled material is, of course, an uncontrollable variable that severely limits the utility of biological treatment. Tables 6 and 7 summarize the findings in the literature relative to potential effectiveness of treatment for different materials.

It is apparent from considerations of the life cycle of bacterial populations applied to a new medium and the lack of control of important variables on which treatment effectiveness depends, that the use of biological agents for mitigation of spills is not appropriate except where the spilled material can be contained for substantial periods of time. The potential for sufficient containment exists for land spills, for spills in small lakes and farm ponds, and probably in small streams that can be temporarily dammed. Perhaps the greatest potential exists at industrial installations that are already equipped with aeration lagoons or settling ponds where cultures of acclimated bacteria may already be present or deliberately maintained.

Bacteria useful in oxidation of hazardous materials include natural cultures in soil and surface waters, sewage sludge, acclimated sewage sludge and special strains being developed commercially.

The problem of producing and storing a large quantity of bacteria species specific for various kinds of hazardous materials is a serious constraint to the use of biological countermeasures. It is desirable, therefore, to find a species of bacteria that is effective for oxidation of a broad spectrum of toxic materials and is relatively easy to produce in large volumes. The pseudomonads have been found to be versatile in this respect. Pseudomonas fluoresceus, for example, will grow on sugars, amino acids, organic acids, aromatic compounds, and other cyclic organic compounds.

A new hybrid bacteria was developed by researchers at General Electric (14) that consumes crude oil at a rate several times greater than other oil degradation bacteria. This bacteria, a Pseudomonas species, was developed when scientists transmitted plasmids containing DNA from oil-consuming bacteria to a single strain. The microorganism has the genetic information to produce digestive enzymes for a variety of hydrocarbon molecules. The implication of this to the future of microbial degradation is that, while at one time mixtures of bacterial strains were applied to the spill, one strain could now be utilized. This eliminated competition for nutrients by the strains, increased efficiency for the treatment, and led to the possibility of developing other single organisms with the ability to degrade a variety of hazardous substances.

For effective utilization of biological media as a spill treatment agent, adequate supplies of microorganisms must be maintained at suitable locations for innoculation of contaminated environment. Activated sludge from sewage treatment plants provide the only readily available source of highly

TABLE 6. BIOLOGICAL OXIDATION
(Quiescent Conditions)

Chemical	% Oxidation	Seed Source	BOD Duration
Benzene	1.9	Sewage sludge	5 days
Benzene	8.0	Acclimated activated sludge	5 days
Ethyl benzene	2.7	Sewage and acclimated activated sludge	5 days
n-Propanol	94	Activated sludge seed	5 days
Acetaldehyde	93	Acclimated activated sludge	5 days
Acrolein	33	Acclimated trickling filter seed	10 days
Formaldehyde (500 mg/l)	47	Acclimated activated sludge	5 days
Formaldehyde (333 mg/l)	94	Acclimated activated sludge	5 days
Furfural	100	Acclimated activated sludge	2 days
Benzoic acid	46	Sewage seed	10 days
Formic acid	40	Activated sludge seed	5 days
Cresols	95-100	Sewage seed	2-7 days
Phenol	42-100	Sewage seed	2-10 days
Acrylonitrile	0-67	Sewage seed	5-10 days
Adiponitrile	40	Sewage seed	5 days
Benzonitrile	40	Sewage seed	5 days
Potassium cyanide	0	Activated sludge seed	7 days

Ref: Ryckman, et al., 1966.

concentrated cultures normally available throughout the country. Armstrong, et al. (15) reported that most of the 20 top-ranked hazardous materials were amenable to oxidation by bacteria from this source. Problems of acclimation still exist, however. Some hydrocarbons (i.e., short chained alkanes) are known to be toxic to microorganisms. Regardless of source or organisms used, the potential success of the specific organism for the treatment of the specific spill in the required time must be established before application to the contaminated region.

TABLE 7. BIOLOGICAL OXIDATION
(Biological Treatment Plant Conditions)

Chemical	% Oxidation	Seed Technique	Respirometer Test Duration
Benzene	3.5-13.0*	Activated sludge	6-192 hours
Chlorobenzene	17.1	Activated sludge	192 hours
Ethylbenzene	8.2-25.2*	Activated sludge	6-192 hours
Styrene	18	Activated sludge	10 hours
Toluene	34.8*	Activated sludge	192 hours
Xylenes	0-35.8*	Activated sludge	192 hours
Propanol	55	Activated sludge	24 hours
Acetaldehyde	49**	Activated sludge	23 hours
Formaldehyde	99	Activated sludge	5 days
Butanoic acid	32.2	Activated sludge	24 hours
Cresol	28.4-36.6*	Activated sludge	192 hours
Phenol	34*	Activated sludge	192 hours
Phenol	39***	Activated sludge	12 hours

* Acclimated to aniline
** Acclimated to ethanol
*** Acclimated to phenol

Ref: Ryckman, et al., 1966.

There are a number of special cultures now marketed and approved for use in treatment of oil discharges (16). The need for acclimation remains a problem for general utilization on hazardous spills.

Bacteria may be stored for long periods of time in the dormant state, in a frozen or lyophilized powder form, which can be reconstituted when needed. Storage in liquid form is also possible and may be desirable because they are ready for immediate application. Storage in the lyophilized form is desirable since bacteria may be left at room temperature, but reconstitution of the powdered culture requires a few hours of preparation time.

Ecological Imbalance and Toxicity

Further limiting to the use of microbial degradation is the introduction of undesirable bacteria to the ecosystem. Toxic effects of these organisms or their competition with normal flora and fauna of the area may lead to an imbalance in the ecology. Other toxicity considerations include the toxicity to

aquatic life of the degradation products and of additives that increase the rate of degradation. The resulting metabolic products of the treated spill may be more toxic and have a greater solubility (17). For example, the conversion of butylbenzene to 3-phenylpropionic acid by a Pseudomonas species resulted in a solubility increase of more than 100 times (60 mg/l to 6000 mg/l).

Ideally, microorganisms used for spill treatment should be uniformly distributed throughout a contaminated liquid medium or over a land surface. Spray application seems most appropriate from a mitigation viewpoint, but harmful effects to human lungs exposed to the spray can be serious. Toxicity of microbes to human and other animal life must be ascertained before treatment. Toxic effects of applied organisms and their competition with natural flora and fauna of the area may lead to imbalance in the ecology.

In addition to the toxicity of the organisms, the toxicity of the degradation products of the spilled material must be considered. The metabolic products of a treated spill can be more toxic and have greater solubility than the original contaminant.

Recommendations

Many materials are amenable to treatment by biological degradation. Table 3 lists substances found to be readily removed from the environment. Many of these appear on the hazardous substance list, i.e., cresol, phenol, and furfural.

Other materials found to be removed by biological degradation with acclimated microorganisms are summarized in Table 4. Those materials not compatible with biological treatment are listed in Table 8. These should not be considered for mitigation by means of degradation.

It is recommended that biological agents be considered appropriate for mitigation of spills of those materials listed in Tables 3 and 4, but only for those cases in which the contaminated medium can be contained. Because of the difficulty in controlling biological processes and variables that affect them, it is recommended that other mitigation agents be used for spill treatment whenever possible.

DISPERSING AGENTS

The use of chemicals to facilitate the action of biological degradation may be considered for hazardous spill treatment, as they have been for oil spills. Dispersants may be added to the spill to increase the surface area available to the organisms for degradation.

Dispersants, which promote the formation of hydrocarbon-in-water suspensions, contain surfactants, solvents, and stabilizers. The surfactants reduce the surface tension of organic material and provide the chemical species necessary to form a molecular layer.

TABLE 8. REPORTED ORGANIC COMPOUNDS RESISTANT TO REMOVAL FROM AQUATIC ENVIRONMENT

Compound	Technique
Hydrocarbons	
Benzene	BOD AS
tert-Butyl benzene	BOD AS
Ethylene chloro-hydrin	BOD AS
n-Dodecane	BOD AS*
Alcohols	
tert-Amylalcohol	BOD AS
2-Hydroxybutanol	BOD AS
Pentaerythritol	Resp. AS
2,2'-Oxydiethanol	BOD AS
Polyethylene glycol 400	BOD AS
Tetraethylene glycol	BOD AS
Aldehydes, Ketones, Acids, Salts, and Ethers	
Croton aldehyde	BOD AS
Methyl vinyl ketone	BOD TF
Thioglycolic acid	Resp. AS
Dioxane	BOD AS
di-Ethylether	BOD AS
bis-2-Ethoxy ethyl ether	BOD AS
Ethyleneglycol diethylether	BOD AS
Polyethylene glycolacetate 400	BOD AS
Nitrogen Compounds	
Acetylmorphine	BOD AS
Cystine	Resp. AS
Thioacetamide	Resp. AS
Triethanolamine	BOD AS
Sulfur Compounds	
sec-Amyl benzene sulfonate	BOD AS
tert-Amyl benzene sulfonate	BOD AS
tert-Butyl benzene sulfonate	BOD AS
tert-Dipropane benzene sulfonate	BOD AS
tert-Pentapropane benzene sulfonate	BOD AS
tert-Tripropane benzene sulfonate	BOD AS
tert-Tetrapropane benzene sulfonate	BOD AS

AS - Activated sludge seed
TF - Trickling filter
AS* - Acclimated activated sludge seed
Resp. - Respirometer
BOD - Biological oxygen demand

Ref: Ryckman, et al., 1966.

The purpose of dispersing agents is primarily to promote biological degradation either with natural biota present or in conjunction with biological treatment agents. Chemical enhancement of the biodegradation of crude oil has been reported by many (18-20). When the watercourse conditions (fast-moving, large-volume river) exist such that containment and removal of hazardous spill is not possible, dispersants may be used to aid in diluting the spilled material to a concentration below its toxic level. The dispersing agent must also be carefully selected in order that additional environmental damage will be minimized.

Many investigations of spill situations have reported that the dispersants used to fight the spill were more toxic than the spilled oil (21, 22). Comparisons of the toxicities of dispersants used to clean the Torrey Canyon oil spill with dispersants developed since the incident revealed that toxic concentrations are many orders of magnitude greater for more recent formulations (22). Research since 1968 has produced formulations containing water or saturated hydrocarbons as solvents.

In addition, consideration must be given to the possibility of creating an oxygen deficit in the water system that may cause indirect biological damage. The addition of chemical dispersants to oil spills was found to produce high values for biological oxygen demand (23). It was estimated that a spill of 75,000 barrels of oil in the Delaware River which was treated with dispersant chemicals would produce an oxygen deficit of 3.4 mg/l O_2 by the third day. No biological stress would be expected unless the percent saturation decreased to 50% (4.6 mg/l).

It may be concluded that properly selected chemical dispersants are compatible with the environment.

Recommendations

The advantage of using dispersants to treat spills are (1) the rate of biodegradation is increased, (2) damage to marine fowl is avoided since oil or other hazardous material is removed from the water surface, (3) the fire hazard from the spill is reduced by dispersion of the hazardous material several feet into the water column, (4) spill is prevented from wetting solid surfaces such as beach sand and shore property.

Dispersants are recommended as desirable additions to enhance the biological degradation of spilled material. However, they must be chosen with care and the amount carefully controlled, to avoid unnecessary harm to aquatic life. Prior to the use of dispersant on a specific spilled substance, it should be established through research that no increase in toxicity will result from the dispersed substance or the degradation product of the added dispersant.

A compendium of information available on dispersing agents was prepared by Battelle (18). As a single source of information, it was intended as an aid in logistic planning and as a reference in an emergency for selection of agents for oil spills. However, it is applicable to other hazardous spills. The compendium summarizes the composition, shelf life, storage requirements, type of oil substrates, and conditions for use of these agents.

PRECIPITATION AGENTS

Many pollutants are ultimately converted in the environment to environmentally acceptable chemicals. Both chemical and biological processes ultimately oxidize most organics to carbon dioxide and water. Metal ions differ from organics in that metal ion spills continue to be an indefinite threat unless they are rendered insoluble by some precipitation or complex reaction.

Precipitation has been shown to be effective in reducing the concentration of metal ions in solution by both hydroxide and sulfide precipitation. Both processes should be considered acceptable for treatment of spills of heavy metal compounds.

Many metallic hydroxides are insoluble in water only at elevated pH. As a water body returns to normal after spill treatment, many hydroxide precipitates will redissolve. Hydroxide precipitation therefore should be limited for spill treatment to those situations in which the precipitate can be mechanically removed from the environment. Thus, utility is limited to land spills or water spills in small ponds.

Sulfide precipitates are usually the least soluble salts of toxic metals. It is therefore permissible to use hydroxide precipitation under some situations in which the precipitate cannot be removed from the watercourse. The limitation is associated primarily with the toxicity of the sulfide ion and the difficulty of controlling application rates to stoichiometric proportions in large spills. It is recommended, therefore, that sulfide precipitation be considered acceptable for use even with the crude controls described herein on small spills of metallic compounds and that its use be limited on large spills only to those situations in which adequate monitoring of the reaction is available.

It is well known that the most insoluble salts of many metals are the sulfides. This is true for most of the metals listed in Table 9. In most cases, sulfides are extremely difficult to solubilize except in extremely acidic media.

Treatment using sulfide ion (S^{--}) can be affected by using such materials as hydrogen sulfide gas or aqueous sodium sulfide as the treatment agent:

$$M^{++} + S^{--} \rightarrow MS\downarrow$$

At concentrations of heavy metal ions that present a toxic hazard, formation of the insoluble metal sulfide proceeds rapidly, and acute toxicity can be reduced within seconds. Sodium sulfide solutions used for treatment are usually stabilized with sodium hydroxide to prevent evolution of toxic hydrogen sulfide fumes. Since the reaction proceeds most rapidly in high-pH media, this stabilization usually promotes even more rapid and efficient reaction.

A wide range of heavy metal compounds can be treated by this sulfide precipitation method. Almost all soluble compounds of the metals listed in Table 9 are subject to sulfide treatment because the sulfide is their least soluble compound whenever excess sulfide ions are available. Sulfide precipitation,

TABLE 9. METAL IONS SUBJECT TO SULFIDE PRECIPITATION

Vanadiam	Tantalum
Manganese	Osmium
Iron	Iridium
Cobalt	Platinum
Nickel	Gold
Copper	Mercury
Zinc	Thallium
Gallium	Lead
Zirconium	Bismuth
Molybdenum	Polonium
Ruthenium	Cerium
Palladium	Arsenic
Silver	Praseodymium
Cadmium	Neodymium
Indium	Thorium
Antimony	Uranium

however, is not effective for treatment of spills of all metal ions, particularly those that are organically complexed or those that are anionic species.

Compounds of chromium, molybdenum, and manganese as the ionic species are difficult to precipitate unless changed into other chemical forms. For example, chromate chrome (CR^{+6}), if first chemically reduced to chromium (Cr^{+3}) with a suitable reducing agent such as sodium thiosulfate, can then be precipitated as the Cr_2S_3 insoluble salt.

Due to the toxicity of the sulfide ion and of any generated hydrogen sulfide gas, the use of sulfide precipitation may require both pre- and post-treatment of the spill and careful control of reagent additions. Pre-treatment would require raising the pH to a point at which sulfide treatment is effective. Alternating use of a solution of sodium sulfide containing a strong base such as caustic soda (NaOH) accomplishes the same purpose. Post-treatment may be necessary to oxidize any unreacted sulfide to the sulfate. Aeration, which occurs naturally in fast-flowing streams, is effective for this purpose.

In the case of small spills (typical of heavy metal discharges), treatment can be monitored on the basis of a simple test : when a small amount of sodium sulfide is injected at the spill site and a visible precipitate forms, additional concentrated sodium sulfide is added until no more precipitate is

formed. This will generally produce a slight excess of sodium sulfide. For large spills, more elaborate monitoring requirements are necessary to prevent inadequate or excessive treatment.

To use sulfide as a mode of spill control, the toxicity of the spilled heavy metal must be compared with the toxicity of the sodium sulfide treatment. When one considers a wide range of metals and their potential toxicity on the basis of volume of water affected, sodium sulfide treatment is approximately 1/20th as toxic as the original metal spilled. Detailed discussion of toxicity considerations associated with sulfide precipitation is presented by Pilié, et al. (2).

The recommended treatment material is a solution of sodium sulfide in water. The solution should be as concentrated as practically possible to conserve space and weight. An aqueous solution of sodium sulfide at 0°C contains 0.85 lbs of sulfide per gallon of water containing 0.04 lbs of sodium hydroxide. The hydroxide is present to retard formation of hydrogen sulfide. Two gallons of this solution are sufficient for the treatment of spills 2 to 10 gallons in size, depending on the heavy metal.

There are some metals that have a tendency to form oxides more readily than the sulfides. These materials are generally easily hydrolyzable and can be treated just with water to render them immobile. Titanium compounds are typical of this group of chemicals. Some hydroxides form at pH below 7. Others, such as nickel (II), iron (II) and manganese (II) require pH values above 9 to be effectively formed. Solubility constants of the hydroxides, however, may be more readily available than large concentrations of sodium sulfide.

Although hydroxide precipitation is not to be considered to be a primary mode of removal of toxic heavy metal ions from large or flowing water bodies, it can be used to immobilize soluble heavy metals in liquid spills upon the land or in a small water body (e.g., farm pond) where the precipitate can be removed. Such treatment could remove the threat of the metal being transported to a water system. Since it is desirable that the pH will revert to neutral conditions under which the metal precipitate will redissolve, removal of the hydroxide precipitate is necessary.

Precipitating agents are effective in decreasing the overall toxicity of a heavy metal spill. However, the precipitated material on the bottom of a lake or stream could exert a toxic effect on the bottom-dwelling organisms. Insoluble mercuric salts can be converted to an organo-mercuric compound by bacterial action. These compounds are more soluble than the inorganic form and do not enter into the food chain. Some heavy metals (i.e., thallium) do not enter into the food chain and are not bioamplified (24). Wilber (25) states that there is not enough data available to determine if precipitated metal salts will re-enter into the environment to be bioamplified. Of the 1300 references in an annotated bibliography on the biological effects of metals in aquatic environment (26), there were no references to the possible chronic effect of insoluble inorganic metal salts.

When the metal salt is not converted to a more toxic organic form and is

sufficiently insoluble, the re-entry of the metal ion would be reduced below a toxic level by dilution in a stream or river. However, in a closed system such as a lake or a pond it is recommended that the precipitated metal salt be removed from the watercourse until the chronic toxic effect of insoluble metal salts is known by further research.

NEUTRALIZING AGENTS

In any spill of an acid or base, regardless of the specific chemicals involved, the potential exists for creating toxic conditions as a result of a pH change. A prime consideration therefore is to adjust the pH in the spill to the environmentally acceptable condition of the natural waterway. Neutralizing agents are those materials that can be used to adjust the pH of a spill plume to the desired environmental value, i.e., to a value between pH 6 and pH 9. Bases may be used to neutralize acidic plumes in which pH less than 7 and acids may be used to neutralize basic plumes in which pH is greater than 7.

Consideration should be given to the treatment of any spill in which the pH is changed markedly from the ambient state. Volume of the spill and the dilution rate of the body of water in which the spill occurred must be considered. Based on fish toxicity studies, spills where the pH has been altered to below pH 6 or above pH 9 must be considered for treatment. A list of common spill acids and bases is included in Table 10.

When to Neutralize

The acids and bases that would be used as neutralizing agents would produce toxic pH conditions if applied to a region that is not affected by the spill or if applied in excess quantities to the spill. In order to avoid treating the wrong portion of a waterway (i.e., missing the spill) or over-treating a spill, it is essential that some method be available to the On-Scene Coordinator (OSC) for measuring pH of the water and monitoring pH changes as treatment progresses.

TABLE 10. COMMONLY SPILLED ACIDS AND BASES

Acetic Acid	Phosphoric Acid
Fatty Acids	Sulfuric Acid
Chlorosulfuric Acid	Sodium Hydroxide
Chromic Acid	Potassium Hydroxide
Formic Acid	Sodium Carbonate
Hydrochloric Acid	Sodium Bicarbonate
Nitric Acid	Calcium Oxide
Perchloric Acid	Calcium Hydroxide

Ground spills must, if possible, be immediately contained. Contained spills on the land can then be removed by physical methods such as shoveling, suction, etc. If physical removal is not possible, neutralization to mitigate ground percolation to the nearest water system must be performed.

It is generally advantageous to neutralize all large spills of acids or bases which occur in water. Neutralization of spills in water should not be attempted, however, unless adequate pH monitoring equipment is available. If only a small quantity of acidic or basic material is spilled in a waterway that provides for rapid dilution to nontoxic pH levels, it may be more appropriate to avoid neutralization, depending on the quality of the system available for monitoring the progress of treatment.

Selection of Neutralization Agents

In general, the chemical reaction involved in neutralization may be written as follows:

$$\text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water}$$

While it is usually the case that the salt ions produced by the reaction are less toxic than the treated spill, options may exist for the OSC to select a neutralizing agent that results in reaction products at minimum toxicity when applied to the spilled material. The reduction in toxicity of a spill plume that can be achieved by neutralization is illustrated in Table 11. In each case shown, the salt produced by the neutralization reaction is substantially less toxic than either the spilled material or the treatment agent. Since the salts are themselves toxic, an important consideration, when a choice of neutralization agent is available, is the selection of the agent that results in the least toxic reaction product. Table 12 illustrates this point. Obviously a substantial toxicity advantage will result if ammonium hydroxide is treated with sulfuric acid rather than the other agents listed. However, it is better to treat with less than ideal agents than not to treat at all. The list of potential neutralization agents presented in Table 13 would generally result in reaction products that are less toxic than the acute pH change produced by spills of concentrate materials against which they may be used.

A final caution is necessary in considering toxicity of reaction products of neutralization. In some cases, such as with a spill of arsenic acid, the salt produced by neutralization will contain a toxic metallic ion. This cannot be avoided in neutralization regardless of agent used. If the pH produced by such a spill is at toxic levels it would be necessary to treat first with a neutralizing agent to eliminate the pH problem and to post-treat with a precipitating agent to remove the metallic ion.

The decision to treat with a neutralization agent is made, therefore, to eliminate toxicity due to pH. Where a choice of neutralization agents is available, it is most important to select the agent that results in the least toxic reaction products. Assuming that several available agents are equally appropriate in this respect, further selection may be based on minimizing the potential for over-treatment and ease of application. These topics are discussed in the following subsections.

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TABLE 11. SULFURIC AND HYDROCHLORIC ACID NEUTRALIZATION

(Critical concentration of each chemical component indicated within parenthesis.)

Sulfuric Acid + Neutralizing Agent	
$H_2SO_4 + Ca(OH)_2$	$CaSO_4 + 2H_2O$
(10 ppm) (18 ppm)	(600 ppm)
$H_2SO_4 + 2NaOH$	$Na_2SO_4 + 2H_2O$
(10 ppm) (20 ppm)	(5000 ppm)
Hydrochloric Acid + Neutralizing Agent	
$2HCL + Ca(OH)_2$	$CaCl_2 + 2H_2O$
(10 ppm) (18 ppm)	(500 ppm)
$HCl + NaOH$	$NaCl + H_2O$
(10 ppm) (20 ppm)	(1000 ppm)

TABLE 12. TOXICITY OF DIFFERENT REACTION PRODUCTS FORMED IN NEUTRALIZATION OF NH_4OH

$NH_4OH + HCl$	$NH_4Cl + HOH$
(15 ppm)(10 ppm)	(160 ppm)
$+ HC_2H_3O_2$	$NH_4C_2H_3O_2 + HOH$
(114 ppm)	(238 ppm)
$- H_2SO_4$	$(NH_4)_2SO_4 + 2H_2O$
(10 ppm)	(> 500 ppm)

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TABLE 13. ACIDS AND BASES SUITABLE FOR SPILL NEUTRALIZATION

Acids	Bases
1. Acidic acid	1. Calcium hydroxide
2. Sulfuric acid	2. Sodium hydroxide
3. Hydrochloric acid	3. Sodium carbonate
	4. Sodium bicarbonate

Strong vs Weak Neutralizing Agents--

To examine the potential for overtreatment of an acid or base spill, it is useful to consider some illustrative titration curves. Such curves illustrate how pH would change as increasing amounts of the neutralizing agent is added. Figure 2 compares typical titration curves that may be expected from treatment of a spill of strong acid with a strong base and with a weak base. It is apparent that during the early stages of treatment there is little or no advantage in using a weak or strong base as treatment material. When approaching the amount of neutralizing agent required for neutralization, the slope of the titration curve increases very rapidly. A small addition of neutralizing agent at this point causes a large change in pH. If a strong base is used for neutralization, the high slope persists until highly toxic values of pH are achieved. If a weak base is being used, the rate of change of pH with additional treatment material begins to decrease when neutrality is reached. The danger of serious overtreatment is thereby reduced. Furthermore, the ultimate pH achieved by massive overdosage of a weak treatment agent, while frequently toxic, is substantially smaller than that achieved by a similar overdose of a strong base. Similar comparisons can be made for treatment of the spill of a strong base with strong or weak acids.

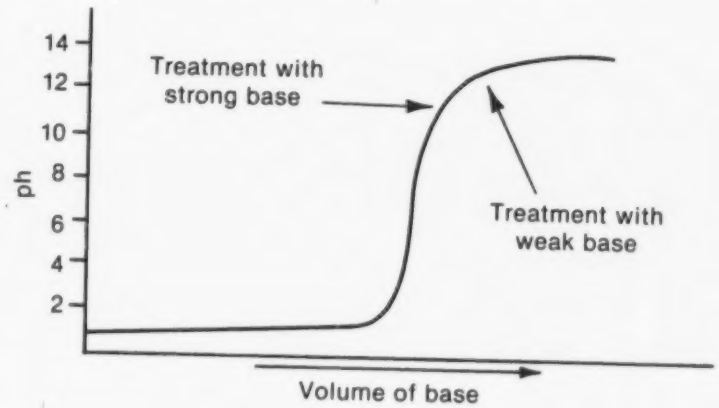

Figure 2. Treatment of strong acid with base.

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Figure 3 presents a comparison of illustrative titration curves that are typical of treatment of a weak acid spill with a strong base and a weak base. As with the treatment of a strong acid, the titration curves for treatment of a weak acid with a strong or weak base are not substantially different during the early stages of treatment.

Once neutrality is achieved, a small addition of a strong base causes a sharp rise in pH to toxic values. The slope of the titration curve for treatment with a weak base begins to decrease shortly after neutrality is achieved. Therefore, the potential for serious overtreatment is substantially reduced. Similar comparisons can be made for treatment of a weak base with strong and weak acids.

Two conclusions can be drawn. First, it is easier to control the treatment operation to avoid overtreatment if weak acids and bases are selected as treatment materials than if strong acids or bases are selected. This does not mean that strong acids or bases should not be used for neutralization when available. It does mean that more careful monitoring is required if the strong materials are used.

A secondary conclusion is that for those occasions when two or more materials are required (because of supply, for example) to neutralize a spill, it is better to use the stronger acid or base during the early stages of treatment and retain the weaker agent to use when neutrality is approached.

Table 13 presents lists of acids and bases that are acceptable neutralizing agents and that are arranged in order of increasing strength. Materials at the top of the lists offer greater ease of operational control and minimum potential for pH overshoot with overtreatment.

Physical Properties of Neutralizing Agents and Reaction Products--

Some of the acids and bases that may be used for spill neutralization are available in both solid and liquid form. In general, much greater control of

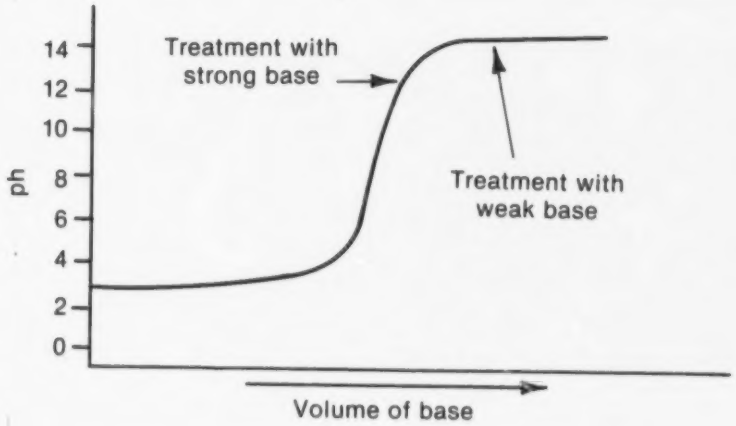

Figure 3. Treatment of a weak acid with base.

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the spill can be obtained through use of liquid phases. In some cases, such as with the use of lime, the solubility of the agent may be so low that operational problems would result from the amount of water that would have to be handled. Under such conditions, a slurry might be used but only with caution. Reaction rates will be retarded and the potential for overtreatment significantly increased.

A wide variety of concentrations of neutralizing agents may be used in spill treatment. In general, the lower the concentration the greater will be the degree of control and uniformity of treatment. In some spills, it may be desirable to use concentrated solutions. For example, if a dense acid such as concentrated sulfuric acid is spilled, it will tend to remain near the bottom of the waterway. Treatment with a concentrated solution of sodium hydroxide would provide similar physical characteristics and increase the probability of mixing of the spilled and neutralizing agent. At substantial downstream distances, the acid may be well mixed in the stream and the use of dilute solutions may be more desirable.

Substantial temperature changes will result from exothermic neutralization when treating highly concentrated spill plumes with concentrated solutions or slurries of neutralizing agents. Treatment should be applied in a controlled manner to avoid sputtering and the danger of serious burns. Minimization of temperature changes will also minimize mixing in the waterbody which, in turn, would minimize plume spread. Use of dilute solutions for treatment will in general minimize these problems but the quantity of treatment material that must be handled becomes extremely large. To avoid, or at least account for, ecological damage due to heating, temperature should be monitored prior to, during, and following neutralization.

Depending on the nature of the spilled and neutralizing agent, some gaseous reaction products may be evolved. Carbon dioxide is usually released when carbonates are involved in the reaction. Deleterious effects of gaseous release may include increased mixing and plume spread, possible frothing, bubbling or sputtering that could cause equipment damage or personnel injury.

When to Stop Treating

Since shock produced by even small pH changes can cause significant ecological damage, it would be ideal to adjust the pH of the spill plume to the value of the unaffected water. Considering the degree of control available in a large-scale field operation, however, and the high slope of the titration curves in near-neutral conditions, the probability of achieving the exact pH desired is small. Since it is desirable to minimize the amount of foreign material in water (either the treatment material or the reaction products), it is generally more desirable to undertreat than to overtreat. Exactly how close the ideal pH should be approached depends on the monitoring network available and the nature of treatment material being used. It is acceptable to stop treatment when the pH of the treated waters is between 6 and 9.

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Recommendations

Neutralization should be considered an acceptable treatment for all spills of acids or bases, provided some method for monitoring pH is available. Whenever possible, neutralization should be accomplished on land spills before the spilled material enters aquiferous or surface water. After the spilled material has entered surface waters, the toxicity associated with the change in pH from natural conditions is usually most critical. Neutralization of spills of large quantities of material is usually appropriate regardless of the neutralization agent available. However, when a choice of agents is available, it is extremely important to select the agent that produces the least toxic reaction products in returning the pH to normal. In some cases, post-treatment for toxic metallic ions may be necessary. All other considerations being equal, some advantage can be obtained by selecting weak agents as opposed to strong agents. Depending on the nature of the spilled material, some advantages can be obtained by selection of neutralization agents with optimum physical characteristics, but it is usually advisable to avoid use of solid agents when possible.

Temperature changes associated with exothermic neutralization reactions can produce secondary thermal pollution, but this problem appears to be of secondary importance. Caution should be observed to avoid personnel injury due to sputtering or bubbling caused by exothermic reactions.

When the monitoring system is not sufficiently accurate to assure treatment to the desired pH, it is usually better to undertreat than to risk overtreatment. pH values between 6 and 9 are acceptable.

OXIDIZING AGENTS

Because of a variety of potential problems with the use of oxidizing agents in spill control, it is recommended that their use be limited to land spills and water spills that are completely contained.

In dilute solutions, oxidation reactions are generally slow. Except in closed systems, they will seldom go to completion. The ultimate products of oxidation of hydrocarbons are CO_2 and H_2O. With complex organic materials, however, the reactions involve several intermediate steps and intermediate reaction products which very probably remain in the environment in open systems and are frequently toxic. To control the reaction and assure that it goes to completion, it is necessary to overtreat to such an extent that severe toxic conditions are produced by the treatment agent.

Oxidation reactions can never be limited to reactions of the agent with the spilled material. Oxidation of natural organic material in the environment, including living organisms, will always accompany oxidation of the spilled pollutant. Thus, valuable organic material is destroyed and the ecological balance is invariably upset.

Because of the utilization of some fraction of the oxidizing agent in reactions with natural organic material, and the inability to drive the reaction with the pollutant to completion, it is impossible to determine the quantity

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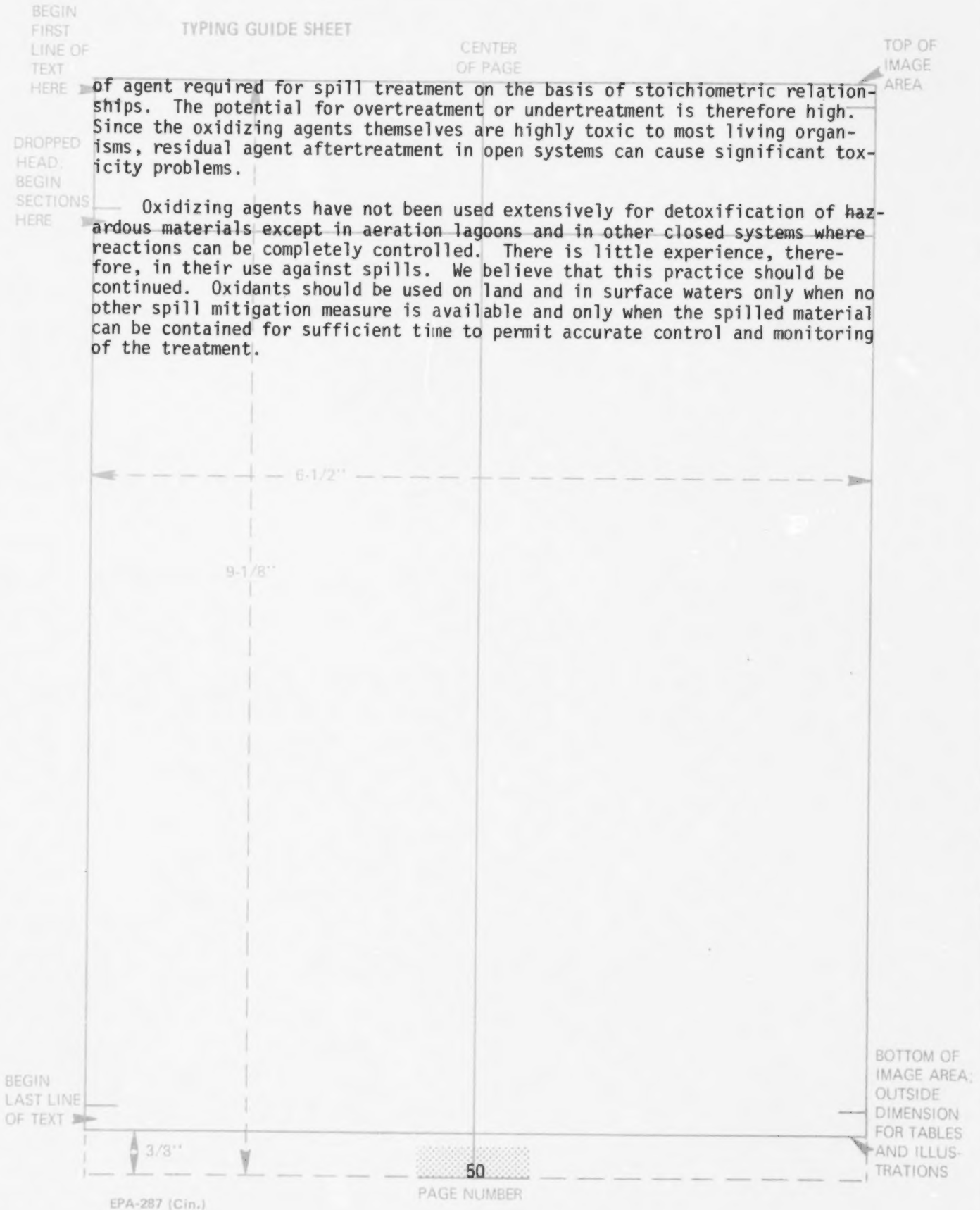

of agent required for spill treatment on the basis of stoichiometric relationships. The potential for overtreatment or undertreatment is therefore high. Since the oxidizing agents themselves are highly toxic to most living organisms, residual agent aftertreatment in open systems can cause significant toxicity problems.

Oxidizing agents have not been used extensively for detoxification of hazardous materials except in aeration lagoons and in other closed systems where reactions can be completely controlled. There is little experience, therefore, in their use against spills. We believe that this practice should be continued. Oxidants should be used on land and in surface waters only when no other spill mitigation measure is available and only when the spilled material can be contained for sufficient time to permit accurate control and monitoring of the treatment.

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SECTION 5

HAZARDOUS SUBSTANCE - COUNTERMEASURE MATRIX

A countermeasure matrix has been generated to reference which classes of mitigation agents are recommended for treating hazardous substances involved in spills near or into a watercourse (Appendix A). The chemicals are listed in alphabetical order in the first column. In the second column, the EPA toxicity classification is listed. The LC_{50} toxic concentration for each category is given in Table 14. The third and fourth column list the density of the hazardous substance and the physical form of the pure hazardous substance, respectively.

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The fifth column is the P/C/D category. The P/C/D category takes into consideration the solubility, density, volatility and the ability to disperse in water of each hazardous substance. The eight P/C/D categories are:

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1. IVF (insoluble volatile floaters)
2. INF (insoluble nonvolatile floaters)
3. IS (insoluble sinkers)
4. SM (soluble mixers)
5. P (precipitator)
6. SS (soluble sinker)

TABLE 14. EPA TOXICITY CATEGORY

Category	Toxicity Range
A	$LC_{50} \leq 1$ ppm
B	1 ppm < $LC_{50} \leq 10$ ppm
C	10 ppm < $LC_{50} \leq 100$ ppm
D	100 ppm < $LC_{50} \leq 500$ ppm

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7. SF (soluble floater)

8. M (miscible)

A complete definition of each category and the hazardous substances within each category is listed in Appendix B.

The remainder of the matrix specifies which categories of countermeasures are effective for controlling hazardous substances discharged on ground or into the watercourse.

The Coast Guard has issued a report that discusses various mitigation agents and methods for hazardous spill control (27). This report classifies the hazardous chemicals on the Coast Guard CHRIS list into categories and discusses methods of mitigation for each class of chemical.

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SECTION 6

MITIGATION AND SELECTION PARAMETERS

The 1972 Federal Water Pollution Control Act amendment of PL 92-500 states that the EPA shall develop and revise the regulation of hazardous substances to include chemicals when discharge into the environment presents a danger to the public welfare. It is recognized that every chemical substance has a potential of being hazardous to the public welfare. However, a set of criteria was derived to determine what chemicals should be designated as hazardous substances.

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Two criteria were proposed to determine if a chemical should be designated as a hazardous substance: the toxicity of the chemical, and the potential for it to be spilled.

The tentative toxicological criteria were stated in the Federal Register on August 22, 1974. The advance notice states: "Any element or compound produced in excess of research quantities possesses sufficient danger potential to be considered as a candidate hazardous substance if it is lethal to: (a) one-half of a test population of aquatic animals in 96 hours or less at a concentration of 500 milligrams per liter (mg/l) or less; or (b) one-half of a test population of animals in 14 days or less when administered as a single oral dose equal to or less than 50 milligrams per kilogram (mg/kg) of body weight; or (c) one-half of a test population of animals in 14 days or less when dermally exposed to an amount equal to or less than 200 mg/kg body weight for 24 hours; or (d) one-half of a test population of animals in 14 days or less when exposed to a vapor concentration equal to or less than 200 cubic centimeters per cubic meter (volume/volume) in air for one hour; or (e) aquatic flora as measured by a 50% decrease in cell count, biomass, or photosynthetic ability in 14 days or less at concentrations equal to or less than 100 mg/l."

The second criterion is the probability that a material will be spilled based on the annual amount produced, methods of transporting, handling and storage of the material, past history of spills, and physical-chemical properties. Some chemicals that were classified hazardous substances because of the toxicity criteria were finally excluded from the hazardous substance classification for the following reasons:

1. No past history of a spill,
2. Low annual production,
3. Limited commercial use or distribution, and

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4. High dollar value to the product.

The EPA has proposed to define a hazardous substance as any material that met the above criteria if the material is discharged into navigable water, adjoining shoreline, into the waters of the contiguous zone from vessels, and onshore or offshore facilities. The proposed list of hazardous substances was published in the Federal Register (Vol. 40, No. 250) on December 30, 1975 (see Appendix A).

The hazardous substance list is subdivided with respect to aquatic toxicity (LC_{50} values for 96-hour exposure) into four categories -- A, B, C, and D, respectively -- as having LC_{50} values of less than 1 ppm, 1 to 10 ppm, 10 to 100 ppm, and 100 to 500 ppm. Pesticides are the most toxic group of chemicals, with over 75% being in Category A, having a toxicity less than 1 ppm. Polar and chlorinated organic compounds have LC_{50} values ranging from less than 1 ppm (e.g., PCB, Acrolin) to greater than 100 ppm (e.g., amines, organic halides). Nonpolar organic chemicals generally have LC_{50} values greater than 10 ppm. Also, inorganic salts are within this same range except for salts of Cd, Mg, As, Cu, and CN.

The 1972 Water Pollution Control Act Amendment gives the EPA the responsibility of removing from the environment the spilled hazardous substance. This responsibility raises many questions on how to effectively remove discharged hazardous substances. The general mitigation procedure consists of three parts: first, to contain the spilled material; second, to counteract the hazardous material either by physical removal or by chemical action, which produces a less toxic substance; and third, cleaning up the spill site after treatment by removing any hazardous byproducts and restoring the area to an environmentally sound state.

There are various parameters involved in each of these steps which enter into the decision-making process on how to counteract a hazardous substance spill, and which countermeasure, if any, should be used.

PHYSICAL-CHEMICAL PARAMETER

The physical-chemical properties of the chemical discharged is a factor in deciding what countermeasure action should be taken. The location of the discharge in the environment and the physical state of the discharge will determine the complexity of the mitigation process. When a solid chemical is spilled on land, the spill is the easiest to mitigate. The spilled material is essentially contained at the spill site, with removal being accomplished by placing the chemical spill into containers for proper disposal or recycling.

When the spilled chemical is in a liquid state, the mitigation process is more complicated. The discharge first must be contained to minimize the environmental contamination. The liquid discharge must not be allowed to spread into the environment either by surface runoff or ground percolation. Once the spill is contained, it may be treated by the appropriate countermeasure. In some cases, such as the use of precipitating agents, the countermeasure will help to contain the hazardous material. If the spill gets into a watercourse, either directly or indirectly from a land discharge site, containment and treatment is more complicated.

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The physical-chemical properties of the chemical discharges must be considered in estimating the environmental harm of the discharge. The EPA has proposed to rank spills in waterways into eight P/C/D categories that depict the potential harm the discharge may have on the environment. The eight P/C/D categories are based on solubility, density, volatility, and the ability to disperse in water. The definition of category and chemicals included in each are presented in Appendix A. The eight material classifications are ranked in increasing order of relative damage potential. This P/C/D factor has a value from 0 to 1 which correlates the potential harm of the eight material classes to the environment.

When the P/C/D factor is combined with the four toxic categories, the potential environmental damage of a given unit of a hazardous substance can be compared. For example, one pound of a chemical that is miscible (P/C/D category M) and in a toxic category A is potentially 5000 times as damaging to the environment as one pound of a chemical that is an insoluble, volatile floater (P/C/D category IVF) and in a toxic category D. Physical, chemical, and dispersal properties and the toxicity of hazardous substances will determine to what extent the material must be removed from the environment (Table 15).

WATERCOURSE PARAMETER

Watercourses can be divided into four general classifications based upon the difficulty of containment and treatment.

1. Small lake or pond
2. Large lake
3. Small stream
4. River

In a pond or small lake, the discharged hazardous material is essentially contained within the boundaries of the body of water. This minimizes the

TABLE 15. RELATIVE POTENTIAL ENVIRONMENTAL DAMAGE OF HAZARDOUS SUBSTANCES

Toxic Category	P/C/D Category							
	IVG	INF	IS	SM	P	SS	SF	M
A	500	1150	1800	2450	3100	3750	4400	5000
B	50	115	180	245	310	375	440	500
C	5	11.5	18	24.5	31	37.5	44	50
D	1	2.3	3.6	4.9	6	7.5	9	10

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potential for environmental damage. Mitigation and removal of the spilled material can then proceed.

When the hazardous material is discharged into a large lake, the environmental damage is ultimately contained to the boundaries of the lake. Treating the enormous volume of water within the lake is not possible. Therefore, the spill must be contained in as small a volume as possible. If the spill is at the shoreline, then the contaminated area will consist of the shoreline and the water in the lake. If a lake spill is away from the shoreline, the contaminated volume of water will expand in an elliptical manner, moving in the direction of the flow of water.

When the hazardous material is discharged into a river or stream, the volume of water contaminated will depend on the geometry of the waterway, the rate and volume of water flow. The geometry of the waterway (straight or winding stream, bottom characteristics, etc.) will have an effect on the mixing of the spilled material with the water. This will influence what, if any, containment procedure can be effectively used. For example, a mitigation procedure for floating substances may not be as effective on a turbulent stream compared with a nonturbulent stream.

Containment of a low-volume waterway may be accomplished by damming or diverting the stream, but this is not feasible for a large river. If the stream and river characteristics forbid containment, then mitigation procedures must be initiated as soon as possible. The decision may be made that no countermeasure treatment should be initiated. This decision would be based on the ability of a waterway (large, turbulent river) to dilute the hazardous substance below its toxic level.

MONITORING

In order to determine the extent that the hazardous substance has affected the environment, there must be adequate monitoring of the spilled material. The use of a computer model (i.e, CHRIS) via telephone communications would give a first-order approximation on the extent that the waterway was affected by the spill.

The input to the model would be the physical-chemical, dispersant and toxic characteristics of the spilled material, the watercourse parameter (flow, direction of flow, width, depth, type of watercourse, etc.) and the elapsed time since the discharge occurred. The computer output would consist of concentration contours that would indicate where the spilled material was, with respect to the discharge site.

The computer model will indicate where chemical monitoring of the spill must take place. Only through an adequate monitoring program can the extent that the watercourse is contaminated, and the hazardous material concentration profile downstream of the spill site, be determined. This information would (1) determine where to initiate containment and mitigation procedures, (2) be a guide in determining the potential environmental harm (i.e., to warn downstream water users), and (3) to update the computer model to determine the effectiveness of treatment and containment procedures.

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The monitoring program must be continued throughout the entire mitigation procedure. The decision to increase or decrease the amount of mitigating agent being used can only be based on the results from a monitoring program. If the location and the concentration of the hazardous material is not known, then the decision on where to treat the spill or how much mitigating agent should be used cannot be made. Thus the effectiveness of a countermeasure can only be determined with proper analytical monitoring.

Spilled hazardous material classified into five groups (inorganic salts, inorganic acids and bases, polar and chlorinated organics, nonpolar organics, and pesticides) have different monitoring requirements. Some of these hazardous materials, such as inorganic acids and bases, can be monitored easily with pH. Heavy metal inorganic salts can be monitored directly with precipitating agents. The nonprecipitating inorganic salts must be monitored by an analytical chemical procedure. This analytical procedure should be a wet analytical or colorimetric procedure.

The monitoring of organic hazardous materials, including pesticides, must use analytical instrumentation. An indirect procedure such as Total Organic Carbon could be used, but is nonspecific. Gas chromatography is preferred as a field monitoring procedure.

TOXICITY PARAMETERS

When a hazardous substance discharge is treated with a countermeasure, one of three situations will occur: (1) you will overtreat the spill, (2) treat the spill enough to render it nontoxic to the environment, or (3) undertreat the spill. The toxic effect of each treatment situation must be considered in the decision to use a specific countermeasure. When the spill is overtreated, the toxicity of the byproducts of the countermeasure, as well as the countermeasure agent, must be considered. When the spill is treated properly, then only the toxicity of the byproducts of the mitigation need be considered. When the spill is undertreated, then the byproducts of the countermeasure and the residual untreated toxic material must be taken into consideration.

When a particular countermeasure is considered to mitigate a spilled hazardous material, the potential that the byproducts of the mitigating agent has upon the environment is an important factor in the decision-making process. In most cases the countermeasure does not physically remove the hazardous material from the environment, but chemically transforms it into a less toxic state.

The persistence and degradation of a byproduct may cause long-term harm to the environment. The degradation may be caused by biological decay, desorption, or solubilization. Biological decay may transform the toxic material into a harmless substance that will not cause further damage to the environment. However, if the toxic byproduct enters into the food chain of aquatic plants and animals, and is bio-amplified, then a serious long-term environmental effect may result. But a byproduct of a countermeasure (e.g., heavy metal which is adsorbed to a mass transfer agent or is an insoluble salt) may be slowly released back into the water and be diluted to such a degree that no long-term toxic effect will be seen. In some cases, the mitigating agent itself is a toxic substance and restraints must imposed on its use. For example,

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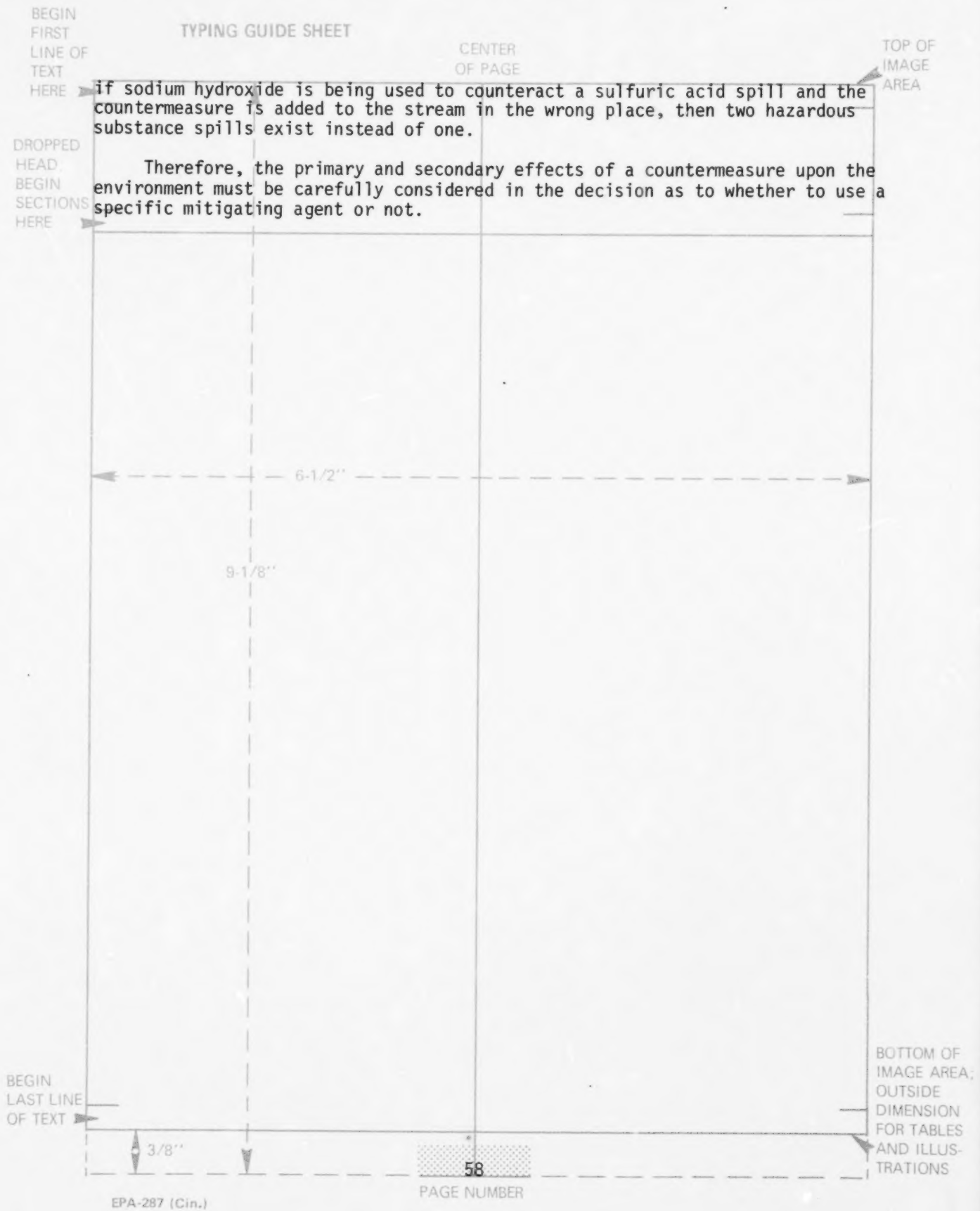
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if sodium hydroxide is being used to counteract a sulfuric acid spill and the countermeasure is added to the stream in the wrong place, then two hazardous substance spills exist instead of one.
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Therefore, the primary and secondary effects of a countermeasure upon the environment must be carefully considered in the decision as to whether to use a specific mitigating agent or not.
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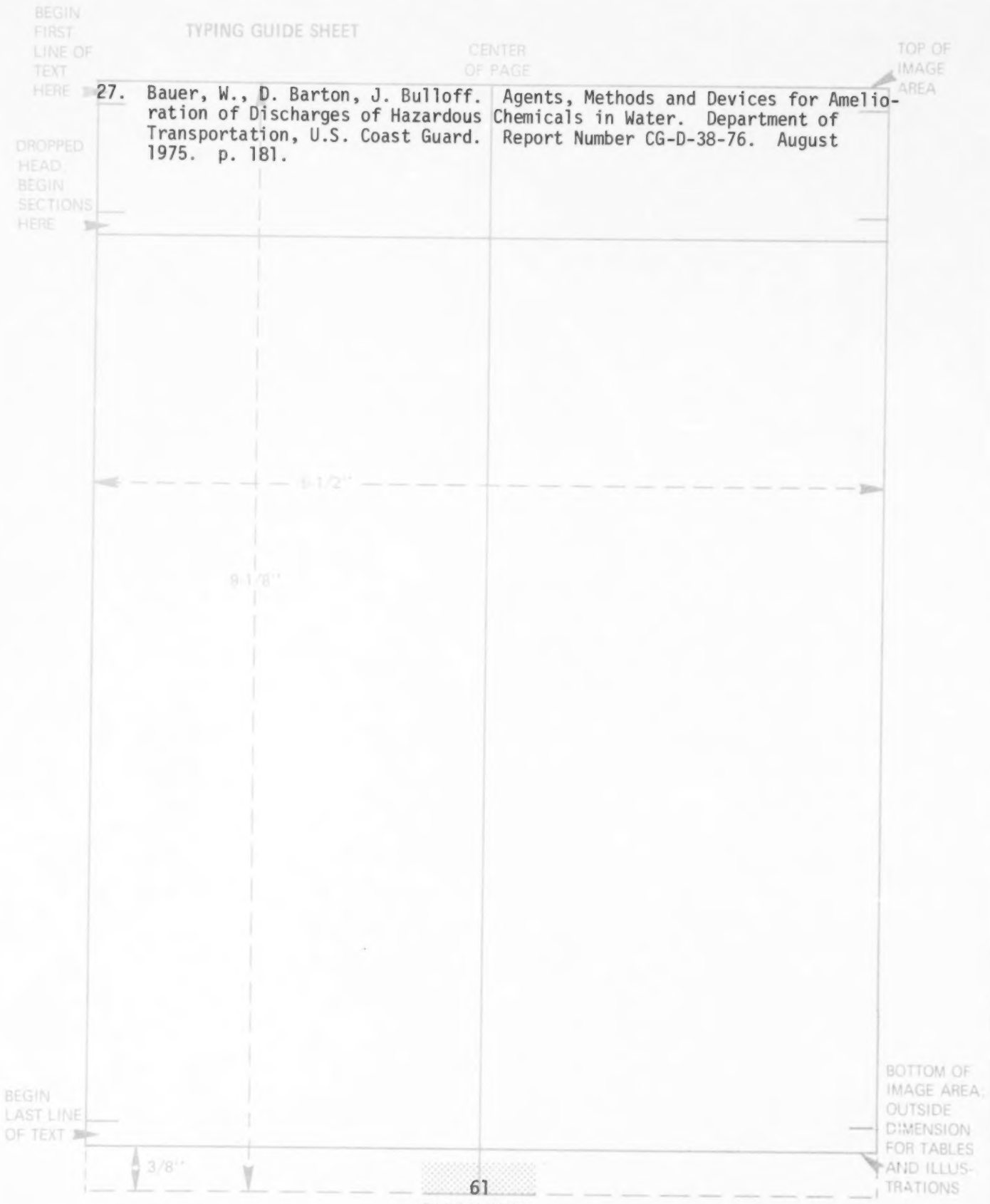

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APPENDIX A. HAZARDOUS SUBSTANCE/COUNTERMEASURE MATRIX

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Acetaldehyde	C	0.783	L	M	x										
Acetic acid	C	1.049	L	M	x				x			x	x		
Acetic anhydride	C	1.083	L	SF	x				x		x	x	x		
Acetone cyanohydrin	C	0.90	L	SF	x				x		x	x	x		x
Acetyl bromide	D	1.52	L	SS	x		x					x	x		x
												x	x		
Acetyl chloride	D	1.11	L	SS	x				x			x	x		
Acrolein	A	0.839	L	SF	x						x	x	x		x
Acrylonitrile	C	0.807	L	SF	x							x	x		x
Adiponitrile	D	0.95	L	SF	x							x	x		x
Aldrin	A	1.65	S	IS	x							x	x		x
Allyl alcohol	B	0.854	L	M	x						x	x	x		
Allyl chloride	C	0.9	L	IVF	x						x	x	x		x
Aluminum Fluoride	D	2.88	S	P	x	x	x			x					
Aluminum sulfate	D	1.69	S	P	x					x					
Ammonia	C	0.60	L	SF	x	x		x				x			x
Ammonium acetate	D	1.073	S	SM	x	x									
Ammonium benzoate	D	1.26	S	SS	x	x	x								
Ammonium bicarbonate	D	1.58	S	SS	x	x									
Ammonium bichromate	D	2.15	S	SS	x	x	x			x					
Ammonium bifluoride	D	1.21	S	SS	x	x	x			x					
Ammonium bisulfite	D	-	S	SS	x	x								x	
Ammonium bromide	D	2.43	S	SS	x	x	x								
Ammonium carbamate	D	-	S	SS	x	x	x								
Ammonium carbonate	S	-	S	SM	x	x									
Ammonium chloride	D	1.53	S	SS	x	x									
Ammonium chromate	D	1.91	S	SS	x	x	x								
Ammonium citrate	D	-	S	SS	x	x									
Ammonium fluoborate	D	1.85	S	SS	x	x	x								

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APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Ammonium fluoride	D	1.31	S	SM	x	x	x			x					
Ammonium hydroxide	C	0.9	S/L	M	x	x		x				x			
Ammonium hypophosphite	D	-	S	SS	x	x									
Ammonium iodide	D	2.56	S	SM	x	x	x								
Ammonium nitrate	D	1.66	S	SM	x	x	x								
Ammonium oxalate	D	1.50	S	SS	x	x	x								
Ammonium pentaborate	D	-	S	SS	x	x	x								
Ammonium persulfate	D	1.98	S	SS	x	x									
Ammonium silicofluoride	C	2.01	S	SS	x	x	x								
Ammonium sulfamate	D	-	S	SM	x	x	x								
Ammonium sulfide	D	1.02	S	SS	x	x	x								
Ammonium sulfite	D	1.41	S	SS	x	x	x							x	
Ammonium tartrate	D	1.61	S	SS	x	x	x							x	
Ammonium thiocyanate	D	1.31	S	SM	x	x	x								
Ammonium thiosulfate	D	-	S	SM	x	x	x								
Amyl acetate	C	0.88	L	INF	x						x	x	x		x
Aniline	C	1.022	L	SS	x						x	x	x		x
Antimony pentachloride	C	2.34	S	P	x	x				x					
Antimony pentafluoride	C	2.99	S	P	x	x	x			x					
Antimony potassium tartrate	C	2.6	S	P	x	x	x			x					
Antimony tribromide	C	4.14	S	P	x	x	x			x					
Antimony trichloride	C	3.14	S	P	x	x				x					
Antimony trifluoride	C	4.38	S	P	x	x	x			x					
Antimony trioxide	C	5.2	S	P	x	x				x					

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APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media: Activated Carbon	Mass Transfer Media: Cationic Resin	Mass Transfer Media: Anionic Resin	Neutralizing Agent: Acid	Neutralizing Agent: Base	Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
Arsenic acid	C	2-2.5	S	P	x		x		x	x		x	x		
Arsenic disulfide	C	3.4	S	IS	x	x	x			x		x	x		
Arsenic pentoxide	B	4.09	S	P	x	x				x					
Arsenic trichloride	C	2.16	S	P	x	x				x					
Arsenic trioxide	B	3.89	S	P	x	x	x			x					
Arsenic trisulfide	B	3.43	S	IS	x	x	x			x					
Barium cyanide	A	-	S	SS	x	x	x			x					
Benzene	C	0.879	L	INF	x									x	
Benzoic acid	D	1.266	S	SS	x							x	x		x
Benzonitrile	C	1.01	L	SS	x				x			x	x		
Benzoyl chloride	D	1.20	L	SS	x							x	x		
Benzyl chloride	D	1.09	L	IS	x							x	x		
Beryllium chloride	D	1.90	S	P	x	x				x					
Beryllium fluoride	C	1.99	S	P	x	x	x			x					
Beryllium nitrate	C	1.56	S	P	x	x				x					
Butyl acetate	C	0.89	L	SF	x										
Butylamine	C	0.74	L	M	x						x	x	x		x
Butyric acid	D	1.00	L	M	x							x	x		
Cadmium acetate	A	2.01	S	SS	x		x		x		x	x	x		x
Cadmium bromide	A	5.19	S	P	x	x				x					
Cadmium chloride	A	4.05	S	P	x	x	x			x					
Calcium arsenate	C	3.0	S	IS	x					x					
Calcium arsenite	C	-	S	SS	x		x			x					
Calcium carbide	D	2.2	S	P	x										
Calcium chromate	D	2.89	S	SS	x		x								
Calcium cyanide	A	-	S	SS	x		x								
Calcium dodecyl-benzene sulfonate	B	-	S	SS	x		x							x	
Calcium hydroxide	D	2.504	S	SS				x							
Calcium hypochlorite	A	2.35	S	SM	x				x						

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APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media: Activated Carbon	Mass Transfer Media: Cationic Resin	Mass Transfer Media: Anionic Resin	Neutralizing Agent: Acid	Neutralizing Agent: Base	Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
Calcium oxide	D	3.40	S	SM	x										
Captan	A	1.5	S	SS	x								x		
Carbaryl	B	-	S	SS	x								x		
Carbon disulfide	C	1.26	L	SS	x							x	x		
Chlordane	A	1.59	L	IS	x							x	x		
Chlorine	A	3.2	L	SF	x										
Chlorobenzene	B	1.1	L	IS	x								x		
Chloroform	B	1.5	L/G	IS	x							x	x		
Chlorosulfonic acid	C	1.8	L	SS	x		x		x			x	x		
Chromic acetate	D	-	S	SS	x	x				x		x	x		
Chromic acid	D	2.7	L	SM	x	x			x	x					
Chromic sulfate	D	1.7	S	SS	x	x				x					
Chromous chloride	D	2.87	S	IS	x	x				x					
Chromyl chloride	D	1.91	S	SS	x	x				x					
Cobaltous bromide	C	2.47	S	P	x	x	x			x					
Cobaltous fluoride	C	4.46	S	P	x	x	x			x					
Cobaltous formate	C	2.13	S	P	x	x				x					
Cobaltous sulfamate	C	-	S	P	x	x				x					
Coumaphos	A	-	S	SS	x										
Cresol	B	1.0	S	SS	x								x		
Cupric acetate	B	1.9	S	P	x	x				x	x	x	x		x
Cupric aceto-arsenite	B	-	S	IS	x	x	x			x					
Cupric chloride	B	3.39	S	P	x	x				x					
Cupric formate	B	1.83	S	P	x	x				x					
Cupric glycinate	B	-	S	P	x	x				x					
Cupric lactate	B	-	S	P	x	x				x					
Cupric nitrate	B	2.32	S	P	x	x				x					
Cupric oxalate	B	-	S	IS	x	x	x			x					
Cupric subacetate	B	1.9	S	P	x	x				x					
Cupric sulfate	B	2.28	S	P	x	x				x					
Cupric sulfate ammoniated	B	-	S	P	x	x				x					
Cupric tartrate	B	-	S	IS	x	x				x					
Cuprous bromide	B	4.72	S	IS	x	x	x			x					

(continued)

APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Cyanogen chloride	A	1.186	G	SS	x	x									
Cyclohexane	C	0.779	L	INF	x										
2,4-D acid	B	0.82	-	IS							x	x	x		x
2,4-D esters	B	-	-	IS									x		
Calapon	B	1.38	L	SS	x								x		
DDT	A	-	S	IS	x							x	x		
Diazinon	A	1.116	L	IS	x							x	x		
Dicamba	C	-	S	SS	x							x	x		
Dichlobenil	C	-	S	SS	x								x		
Dichlone	A	-	S	SS	x								x		
Dichlorvos	A	-	L	SS	x							x	x		
Dieldrin	A	1.75	S	SS	x								x		
Diethylamine	C	0.71	L	SF	x								x		
Dimethylamine	C	0.68	L	SF	x						x	x	x		x
Dinitrobenzene	C	1.54	L	SS	x						x	x	x		x
Dinitrophenol	B	1.68	L	SS	x						x	x	x		x
Diquat	C	-	S	SS	x						x	x	x		x
Disulfoton	A	1.14	L	SS	x								x		
Diuron	B	-	S	SS									x		
Dodecylbenzene-sulfonic acid	B	-	L	SS	x		x				x	x	x		x
Dursban	B	-	-	SS	x										
Endosulfan	A	-	S	SS	x								x		
Endrin	A	-	S	IS	x								x		
Ethion	A	1.22	L	SS	x								x		
Ethylbenzene	C	0.958	L	INF	x							x	x		
Ethylenediamine	C	0.96	L	SF	x						x	x	x		x
EDTA	D	-	S	IS	x						x	x	x		x
Ferric ammonium citrate	C	-	S	P	x	x	x			x	x		x		x
Ferric ammonium oxalate	C	-	S	P	x	x				x					
Ferric chloride	C	2.89	S	P	x	x				x					
Ferric fluoride	C	3.52	S	P	x	x	x			x					
Ferric nitrate	C	1.68	S	P	x	x				x					
Ferric sulfate	C	2.0	S	P	x	x				x					
Ferrous ammonium sulfate	C	1.87	S	P	x	x	x			x					
Ferrous chloride	C	1.93	S	P	x	x				x					
Ferrous sulfate	C	1.899	S	P	x	x				x					
Formaldehyde	C	0.815	L	M	x		x				x	x	x		x

(continued)

APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media: Activated Carbon	Mass Transfer Media: Cationic Resin	Mass Transfer Media: Anionic Resin	Neutralizing Agent: Acid	Neutralizing Agent: Base	Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
Mercuric sulfate	A	6.47	S	P	x	x				x			x		
Mercuric thiocyanate	A	-	S	IS	x	x	x			x			x		
Mercurous nitrate	A	4.79	S	P	x	x				x			x		
Methoxychlor	A	1.41	S	IS	x								x		
Methyl mercaptan	B	0.87	L/G	INF	x							x	x		x
Methyl methacrylate	D	0.936	L	INF	x							x	x		x
Methyl paration	B	1.358	L	IS	x										
Mevinphos	A	-	L	M	x							x	x		
Monoethylamine	C	1.01	-	M	x							x	x		x
Monomethylamine	C	-	-	SF	x								x		x
Naled	A	-	S/L	IS	x										
Naphthalene	B	1.162	S	IS	x							x	x		
Napthenic acid	A	1.4	S	SS	x								x		
Nickel ammonium sulfate	D	1.92	S	P	x	x				x		x	x		
Nickel chloride	D	3.55	S	P	x	x				x					
Nickel formate	C	2.15	S	P	x	x				x					
Nickel hydroxide	C	4.36	S	IS	x	x									
Nickel nitrate	D	2.05	S	P	x	x				x					
Nickel sulfate	D	1.948	S	P	x	x				x					
Nitric acid	C	1.502	L	M	x				x			x			
Nitrobenzene	D	1.19	L	SS	x							x	x		
Nitrogen dioxide	C	1.448	L/G	M	x										
Nitrophenol	B	1.4	L	SS	x						x	x	x		x
Paraformaldehyde	C	1.46	S	SS	x								x		x
Parathion	A	1.26	L	IS	x						x	x	x		
Pentachlorophenol	A	1.978	S	IS	x							x	x		
Phenol	B	1.071	S	SS	x		x				x	x	x	x	
Phosgene	D	1.392	G/L	SS	x								x		x
Phosphoric acid	D	1.834	L	M	x				x			x	x		
Phosphorus	A	1.8-2.7	S	IS								x			
Phosphorous oxychloride	D	1.67	L	SS	x	x									
Phosphorous pentasulfide	C	2.03	S	SS	x										
Phosphorous trichloride	D	1.574	S	SS	x	x	x								

(continued)

APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media					Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Neutralizing Agent: Acid	Neutralizing Agent: Base						
Formic acid	C	1.22	L	M	x										
Fumaric acid	D	1.635	L	SS	x				x		x	x	x		x
Furfural	C	1.15	L	SS	x				x		x	x	x		x
Guthion	A	1.44	L	IS	x						x	x	x		x
Heptachlor	A	1.58	S	IS	x							x	x		
													x		
Hydrochloric acid	D	1.00	L	SS	x		x		x						
Hydrofluoric acid	D	1.15	L	M	x		x		x			x	x		
Hydrogen cyanide	A	0.70	L/G	M	x							x	x		
Hydroxylamine	D	1.23	S	SS	x		x		x			x	x	x	
Isoprene	C	0.681	L	IVF	x								x		
											x	x	x		x
Isopropanolamine dodecylbenzenesulfonate	B	0.90	L	SS	x						x	x	x		x
Kelthane	C	-	-	IS	x										
Lead acetate	D	2.25	S	P	x	x	x						x		
Lead arsenate	D	7.8	S	IS	x	x	x			x					
Lead chloride	D	5.85	S	P	x	x				x					
										x					
Lead fluborate	D	-	S	P	x	x	x			x					
Lead fluoride	C	8.2	S	IS	x	x	x			x					
Lead iodide	D	6.16	S	IS	x	x	x			x					
Lead nitrate	D	4.53	S	P	x	x	x			x					
Lead sterate	D	1.4	S	P	x	x				x					
										x					
Lead sulfate	D	6.2	S	IS	x	x				x					
Lead sulfide	C	7.1	S	IS	x	x	x			x					
Lead tetraacetate	D	2.23	S	P	x	x				x				x	
Lead thiocyanate	D	3.8	S	IS	x	x				x					
Lead thiosulfate	D	5.18	S	IS	x	x				x					
Lead tungstate	D	8.24	S	IS	x	x	x			x					
Lindane	A	1.87	S	SS	x										
Lithium bichromate	D	2.34	S	SM	x	x	x			x			x		
Lithium chromate	D	-	S	SM	x	x	x			x					
Malathion	A	1.23	L	SS								x	x		
Maleic acid	D	1.59	S	SS	x				x		x		x		x
Maleic anhydride	D	0.934	S	SF	x				x		x		x		x
Mercuric acetate	A	3.25	S	P	x	x				x			x		
Mercuric cyanide	A	4.09	S	P	x	x	x			x			x	x	
Mercuric nitrate	A	4.3	S	P	x	x				x			x		

(continued)

APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Polychlorinated biphenyls	A	-	S	IS									x		
Potassium arsenate	C	2.87	S	P	x		x								
Potassium arsenite	C	-	S	P	x		x								
Potassium bichromate	D	2.68	S	SS	x		x								
Potassium chromate	D	2.73	S	SS	x		x								
Potassium cyanide	A	1.52	S	SS	x		x							x	
Potassium hydroxide	C	2.04	S	SM	x			x							
Potassium permanganate	B	2.7	S	SS	x		x								
Proprionic acid	D	0.993	L	M	x				x		x	x	x		x
Proprionic anhydride	D	1.013	L	M	x				x		x	x	x		x
Propyl alcohol	D	0.8	L	M	x										
Pyrethrins	C	-	L	SS							x	x	x		x
Quinoline	A	1.09	L	SS	x							x	x		
Resorcinol	B	1.27	S	SS	x							x	x		x
Selenium oxide	C	3.954	S	SS	x	x				x	x		x		
Sodium	C	0.971	S	SS											
Sodium arsenate	C	1.76	S	SS	x		x								
Sodium arsenite	C	1.87	S	SS	x		x								
Sodium bichromate	D	2.52	S	SM	x	x									
Sodium bifluoride	D	2.08	S	SS	x		x			x					
Sodium bisulfite	D	1.48	S	SS	x		x							x	
Sodium chromate	D	1.483	S	SS	x		x								
Sodium cyanide	A	1.48	S	SS	x		x							x	
Sodium dodecyl-benzene sulfonate	B	-	S	SS	x		x				x		x		x
Sodium fluoride	D	2.78	S	SS	x		x			x					
Sodium hydrosulfide	D	-	S	SS	x		x						x		
Sodium hydroxide	C	2.13	L	SS	x			x				x			

(continued)

APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media: Activated Carbon	Mass Transfer Media: Cationic Resin	Mass Transfer Media: Anionic Resin	Neutralizing Agent: Acid	Neutralizing Agent: Base	Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
Sodium hypochlorite	A	-	S	SM	x		x								
Sodium methylate	C	2.4	S	SS	x		x				x		x		x
Sodium nitrite	B	2.17	S	SS	x										
Sodium phosphate monobasic	D	2.04	S	SS	x										
Sodium phosphate dibasic	D	2.06	S	SM	x										
Sodium phosphate tribasic	D	1.5	S	SS											
Sodium selenite	C	1.63	S	SS			x								
Sodium sulfide	C	1.856	S	SS	x		x			x				x	
Stannous fluoride	D	2.79	S	SS		x	x			x					
Strontium chromate	D	-	S	IS	x	x	x			x					
Strychnine	C	1.36	S	SS	x				x			x	x		x
Styrene	C	0.909	L	INF	x				x			x	x		
Sulfuric acid	C	1.834	L	M	x										
Sulfur monochloride	D	1.69	S	SS	x										
2,4,5-T acid	A	-	S	IS											
2,4,5-T esters	A	-	S	IS											
TDE	A	-	S	IS	x										
Tetraethyl lead	A	1.659	L	IS	x										
Tetraethyl pyrophosphate	B	1.2	L	M	x							x	x		
Toluene	C	0.86	L	INF	x							x			
Toxaphene	A	1.66	L	IS	x						x	x	x		x
Trichlorfon	B	1.73	S	SS	x							x	x		
Trichlorophenol	A	1.1	L	IS	x										
Triethanolamine dodecylbenzene-sulfonate	B	-	L	SS	x							x	x		
Triethylamine	C	1.13	L	SF	x							x	x		
Trimethylamine	C	0.66	L	SF	x						x	x	x		x
Uranium peroxide	D	2.5	S	IS	x	x				x	x	x	x		x
Uranyl acetate	D	2.89	S	P	x	x				x					
Uranyl nitrate	D	2.80	S	P	x	x				x					
Uranyl sulfate	D	3.28	S	P	x	x				x					
Vanadium pentoxide	C	3.36	S	P	x	x				x					
Vanadyl sufate	C	-	S	P	x	x				x					
Vinyl acetate	C	0.94	S	SF	x						x	x	x		x
Xylene	C	0.86	L	INF	x							x	x		x
Xylenol	C	1.02	L	SS	x							x	x		

(continued)

APPENDIX A (CONTINUED)

Material	EPA Category	Density	Physical Form	P/C/D Category	Mass Transfer Media			Neutralizing Agent		Precipitating Agent	Biological Treatment Agent	Gelling Agent	Absorbing Agent	Oxidizing Agent	Dispersing Agent
					Activated Carbon	Cationic Resin	Anionic Resin	Acid	Base						
Zectran	C	-	-	SS	x										
Zinc acetate	C	1.735	S	P	x	x				x			x		
Zinc ammonium chloride	C	1.80	S	P	x	x	x			x					
Zinc bichromate	C	-	S	P	x	x	x			x					
Zinc borate	C	3.64	S	P	x	x	x			x					
Zinc bromide	C	4.22	S	P	x	x	x			x					
Zinc carbonate	C	4.42	S	IS	x	x				x					
Zinc chloride	C	2.907	S	P	x	x				x					
Zinc cyanide	A	1.85	S	IS	x	x	x			x				x	
Zinc fluorodie	C	4.84	S	P	x	x	x			x					
Zinc formate	C	2.21	S	P	x	x				x				x	
Zinc hydrosulfite	C	-	S	P	x	x	x			x					
Zinc nitrate	C	2.07	S	P	x	x				x				x	
Zinc phenol-sulfonate	C	-	S	P	x	x	x			x					
Zinc phosphide	C	4.55	S	IS	x	x	x			x					
Zinc potassium chromate	C	-	S	IS	x	x	x			x					
Zinc sulicofluoride	C	2.1	S	P	x	x	x			x					
Zinc sulfate	C	3.54	S	P	x	x				x					
Zinc sulfate monohydrate	C	3.28	S	P	x	x				x					
Zirconium acetate	D	-	S	P	x	x				x					
Zirconium nitrate	D	-	S	P	x	x				x					
Zirconium oxychloride	D	-	S	P	x	x				x					
Zirconium potassium fluoride	D	-	S	P	x	x				x					
Zirconium sulfate	D	3.22	S	P	x	x				x					
Zirconium tetrachloride	D	2.8	S	P	x	x				x					

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APPENDIX B

HAZARDOUS CHEMICALS CLASSIFIED ACCORDING TO P/C/D CATEGORY

Category IVF: Insoluble volatile floater - material lighter than water with a vapor pressure greater than 20 mmHg and a solubility of less than 1000 ppm, or materials with vapor pressure greater than 100 ppm and solubility less than 10,000 ppm.

Allyl chloride
Benzene
Cyclohexane
Isoprene
Methyl mercaptan
Methyl methacrylate
Styrene
Toluene

Category INF: Insoluble nonvolatile floater - material lighter than water with vapor pressure less than 10 mmHg and solubility less than 1000 ppm.

Amyl acetate
Xylene
Ethylbenzene

Category IS: Insoluble sinker - material heavier than water and solubility less than 1000 ppm.

Aldrin
Arsenic disulfide
Benzyl chloride
Calcium arsenate
Chlorobenzene
Chloroform
Chromous chloride
Cupric acetoarsenite
Cupric oxalate
Cupric tartrate
Cuprous bromide
2,4-D acid
2,4-D esters
Diazinon
EDTA
Guthion
Heptachlor
Kelthane
Lead arsenate
Lead fluroide
Lead iodide
Lead sulfate
Lead thiosulfate
Lead tungstate
Methoxychlor
Methyl parathion
Naled
Naphthalene
Nickel hydroxide
Parathion
Pentachlorophenal
Phosphorus
Polychlorinated biphenyls
Strontium chromate
Strychnine
2,4,5-T acid
2,4,5-T esters
TDE
Tetraethyl lead
Toxaphene
Trichlorophenol
Uranium peroxide
Zinc carbonate
Zinc cyanide

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Lead sulfide
Lead thiocyanate
Zinc phosphide
Zinc potassium chromate

Category SM: Soluble mixers - solid substances that have a solubility greater than 1000 grams per liter of water.

Ammonium acetate
Ammonium sulfamate
Ammonium thiocyanate
Ammonium thiosulfate
Calcium hypochloride
Calcium oxide
Chromic acid
Lithium bichromate
Lithium chromate
Potassium hydroxide
Sodium bichromate
Sodium hypochlorite
Sodium phosphate, dibasic

Category P: Precipitator - salts that dissociate or hydrolyze in water with subsequent precipitation of a toxic ion.

Aluminum fluoride
Aluminum sulfate
Antimony pentachloride
Antimony pentafluoride
Antimony potassium tartrate
Antimony tribromide
Antimony trichloride
Antimony trifluoride
Antimony trioxide
Arsenic acid
Arsenic pentoxide
Arsenic trichloride
Arsenic trioxide
Beryllium chloride
Beryllium fluoride
Beryllium nitrate
Cadmium bromide
Cadmium fluoride
Calcium carbide
Cobaltous bromide
Cobaltous fluoride
Cobaltous formate
Cobaltous sulfamate
Cupric acetate
Cupric chloride
Cupric formate
Cupric glycinate
Cupric lactate
Cupric nitrate
Cupric subacetate
Cupric sulfate
Cupric sulfate ammoniated
Ferric ammonium citrate
Ferric ammonium oxalate
Ferric chloride
Ferric fluoride
Ferric nitrate
Ferric sulfate
Ferrous ammonium sulfate
Ferrous chloride
Ferrous sulfate
Lead acetate
Lead chloride
Lead fluoborate
Lead nitrate
Lead stearate
Lead tetracetate
Mercuric acetate
Mercuric cyanide
Mercuric nitrate
Mercuric sulfate
Mercurous nitrate
Nickel ammonium sulfate
Nickel chloride
Nickel formate
Nickel nitrate
Nickel sulfate
Potassium arsenate
Potassium arsenite
Uranyl acetate
Uranyl nitrate
Uranyl sulfate
Vanadium pentoxide
Vanadium sulfate
Zinc acetate
Zinc ammonium chloride
Zinc bichromate
Zinc borate
Zinc bromide
Zinc chloride
Zinc fluoride
Zinc formate
Zinc hydrosulfide
Zinc nitrate
Zinc phenolsulfonate
Zinc silicofluoride
Zinc sulfate
Zinc sulfate, monohydrate
Zirconium acetate
Zirconium nitrate
Zirconium oxychloride
Zirconium potassium fluoride
Zirconium sulfate
Zirconium tetrachloride

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Category SF: Soluble floaters - material lighter than water and of a solubility greater than 1000 ppm.

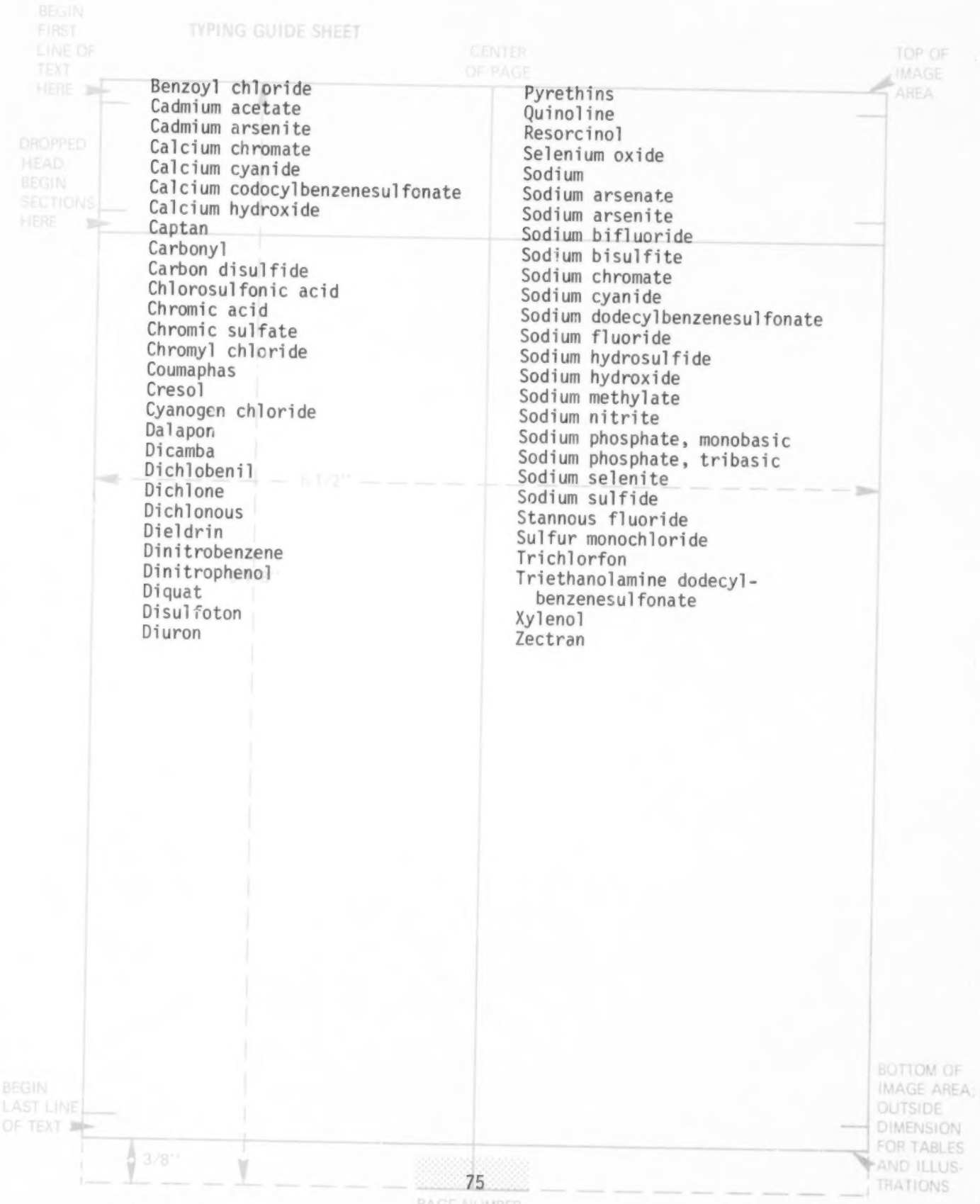
Acetic anhydride
Acetone cyanohydrin
Acrolein
Acrylonitrile
Adiponitrile
Ammonia
Butyl acetate
Chlorine
Diethylamine
Dimethylamine
Ethylenediamine
Maleic anhydride
Monoethylamine
Trimethylamine
Vinyl acetate

Category M: Miscible - liquids that are free to mix with water in any proportion.

Acetaldehyde
Acetic acid
Allyl alcohol
Ammonium hydroxide
Butylamine
Butyric acid
Formaldehyde
Formic acid
Hydrofluoric acid
Hydrogen cyanide
Mevinphos
Monoethylamine
Nitric acid
Nitrogen dioxide
Phosphoric acid
Proprionic acid
Proprionic anhydride
Propyl alcohol
Sulfuric acid
Tetraethyl pyrophosphate

Category SS: Soluble sinkers - materials heavier than water and of solubility greater than 1000 ppm.

Acetyl bromide
Acetyl chloride
Ammonium benzoate
Ammonium bicarbonate
Ammonium bichromate
Ammonium bifluoride
Ammonium bisulfite
Ammonium bromide
Ammonium carbamate
Ammonium chloride
Ammonium chromate
Ammonium citrate
Ammonium fluoborate
Ammonium hypophosphate
Ammonium oxalate
Ammonium pentaborate
Ammonium persulfate
Ammonium silicofluoride
Ammonium sulfide
Ammonium sulfite
Ammonium tartrate
Aniline
Barium cyanide
Benzoic acid
Benzonitrile
Dodecylbenzenesulfonic acid
Duraban
Endosulfan
Ethion
Fumaric acid
Furfural
Hydrochloric acid
Hydroxylamine
Isopropanolamine dodecylbenzenesulfonate
Lindane
Malathion
Maleic acid
Naphtheric acid
Nitrogenzene
Nitrophenol
Paraformaldehyde
Phenol
Phosgene
Phosphorous oxychloride
Phosphorous pentrasulfide
Phosphorous trichloride
Potassium bichromate
Potassium chromate
Potassium cyanide
Potassium permanganate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Benzoyl chloride
Cadmium acetate
Cadmium arsenite
Calcium chromate
Calcium cyanide
Calcium codocylbenzenesulfonate
Calcium hydroxide
Captan
Carbonyl
Carbon disulfide
Chlorosulfonic acid
Chromic acid
Chromic sulfate
Chromyl chloride
Coumaphas
Cresol
Cyanogen chloride
Dalapon
Dicamba
Dichlobenil
Dichlone
Dichlonous
Dieldrin
Dinitrobenzene
Dinitrophenol
Diquat
Disulfoton
Diuron
Pyrethins
Quinoline
Resorcinol
Selenium oxide
Sodium
Sodium arsenate
Sodium arsenite
Sodium bifluoride
Sodium bisulfite
Sodium chromate
Sodium cyanide
Sodium dodecylbenzenesulfonate
Sodium fluoride
Sodium hydrosulfide
Sodium hydroxide
Sodium methylate
Sodium nitrite
Sodium phosphate, monobasic
Sodium phosphate, tribasic
Sodium selenite
Sodium sulfide
Stannous fluoride
Sulfur monochloride
Trichlorfon
Triethanolamine dodecyl-benzenesulfonate
Xylenol
Zectran
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